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# CATALYTIC PROCESSES IN APPLIED CHEMISTRY

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# CLASSIFIED LIST OF PROCESSES DEALT WITH IN SECTIONS II TO IV

	Catalyst.	Sect.	
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"    "    hydrocarbons . . . . .	Nickel, alumina.	II.	2 90
"    "    water (Bergius) . . . . .	Iron.	II.	2 94
Water-gas, etc., catalyses . . . . .		II.	3 97
Production of methane . . . . .	Nickel, MoS <sub>2</sub> .	II.	3 97
Detoxification of town's gas . . . . .	Nickel.	II.	3 101
Purification of hydrogen (removal of carbon monoxide) . . . . .	Mixed metallic oxides.	II.	3 104
Production of methyl alcohol . . . . .	Zinc chromates.	II.	3 105
"    "    higher alcohols . . . . .	Iron-alkali, etc.	II.	3 110
"    "    acetic acid. . . . .	Phosphoric acid, etc.	II.	3 114
"    "    hydrocarbons (motor spirit). . . . .	Cobalt-thorium oxide.	II.	115
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Dehydrogenation of alcohols . . . . .	Copper.	II.	10 241
Hydrogenation of aldehydes or ketones . . . . .	Nickel.	II.	10 250
Dehydration of alcohols . . . . .	Metallic oxides.	II.	10 254
Production of ketones from acids. . . . .	Metallic oxides.	II.	10 258
Production of acetone from alcohol or acetylene and steam. . . . .	Iron-alkali ; mixed oxides.	II.	10 260
Oxidation of hydrocarbons, etc. . . . .	Vanadium or molybdenum oxides.	II.	10 263

Process.	Catalyst.	Sect.	Chap.	Page.
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Production of motor spirit and other hydrocarbon products from coal, tars or mineral oils.	Iron; tin; sulphides and oxides of Mo and W.	II.	4	128
Hydrogenation of fats	Nickel; palladium, etc.	II.	11	276
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Alcohols from olefines	Sulphuric acid.	IV.	1	387
Hydrolytic actions:				
Starch into glucose and other sugars.	Mineral acids.	IV.	2	395
Cellulose into fermentable sugars	Mineral acids.	IV.	2	397
Fats	Lime, etc.; Twitchell agent; acids.	IV.	2	400
Benzaldehyde and benzoic acid from chlorinated toluene.	Iron.	IV.	2	404



# CLASSIFIED LIST OF PROCESSES xi

Process.	Catalyst.	Sect.	Chap.	Page.
<b>Esterification and dehydration :</b>				
Esters (using organic acid)	Sulphuric acid ; hydrochloric acid.	IV.	3	409
Acetates (using acetic anhydride)	Sulphuric acid ; anhydrous sodium acetate or zinc chloride.	IV.	3	411
Acetals	Mineral acids ; calcium chloride.	IV.	3	414
Ether	Sulphuric acid.	IV.	3	414
Ethylene	Sulphuric or phosphoric acids.	IV.	3	417
Glycol ethers.	Fuller's earth.	IV.	3	418
<b>Condensation :</b>				
Ionones, etc.	Alkalies ; acids.	IV.	4	422
Resins (bakelite, etc.)	Alkalies ; acids.	IV.	4	424
Friedel and Crafts synthesis	AlCl <sub>3</sub> , FeCl <sub>3</sub> , ZnCl <sub>2</sub> .	IV.	4	431
Sandmeyer and Gattermann syntheses	Copper ; copper salts.	IV.	4	434
Chlorination of organic compounds	FeCl <sub>3</sub> ; PCl <sub>3</sub> ; S ; SbCl <sub>5</sub> .	IV.	4	437
Oxidation.	Pb, Mn and Co linoleates and abietates ; compounds of Mn, V, Os, Hg, etc.	IV.	4	440
Sulphonation	Mercury sulphate ; iodine or hydriodic acid ; salts of copper.	IV.	4	442
Rubber accelerators	Various.	IV.	4	443
<b>Polymerisation :</b>				
Production of synthetic rubber	Sodium ; peroxides and perborates.	IV.	5	451
" " " resins	Mineral acids ; alkali metals ; peroxides.	IV.	5	454
" " lubricants	Aluminium chloride ; boron trifluoride.	IV.	5	456
" " motor spirit	Phosphoric acids	IV.	5	457

# CLASSIFIED LIST OF PRODUCTS DEALT WITH IN SECTIONS II- TO IV

## I. Inorganic Compounds

Product.	From.	Catalyst.	Sect.	Chap.	Page.
Ammonia .	Nitrogen and hydrogen.	Iron-alkali.	II.	5	155
Carbon dioxide .	Carbon monoxide	Metallic oxides .	II.	2	104
Carbonyl chloride	Chlorine and carbon monoxide.	Active charcoal .	II.	12	315
Chlorine .	Hydrochloric acid	$\text{CuCl}_2$ ; $\text{MgOCl}_2$ ; $\text{MnO}_2$ .	II.	8	224
Cyanamide .	Carbide and nitrogen.	Alkali halides .	II.	5	170
Hydrochloric acid	Chlorine and hydrogen.	Active charcoal .	II.	12	316
Hydrogen .	Hydrocarbons .	Nickel and alumina	II.	2	90
" "	Water-gas .	Iron .	II.	2	80
" "	Water ; water-gas.	" "	II.	2	94
Hydrogen cyanide	Carbon monoxide or hydrocarbons and ammonia.	Metallic oxides .	II.	5	174
Nitric acid .	Ammonia .	Platinum ; iron-bismuth oxides, etc.	II.	6	181
Sulphuric acid .	Sulphur dioxide .	Nitrogen oxides (chamber).	II.	7	211
" "	" "	Platinum ; iron oxide ; vanadium oxide (contact).	II.	7	203
Sulphuryl chloride	Chlorine and sulphur dioxide.	Active charcoal .	II.	12	316

## II. Organic Compounds

Product.	From.	Catalyst.	Sect.	Chap.	Page.
Acetal .	Acetaldehyde .	Hydrogen chloride ; calcium chloride.	IV.	3	414
Acetaldehyde .	Acetylene .	Mercury salts .	IV.	1	370
" "	Ethyl alcohol .	Copper .	II.	10	248
Acetic acid .	Acetaldehyde .	Manganese acetate	IV.	1	381
" "	Alcohol .	Fermentation .	III.	3	343

# CLASSIFIED LIST OF PRODUCTS xiii

Product.	From.	Catalyst.	Sect.	Chap.	Page.
Acetic acid	Cellulose	Fermentation	III.	4	356
"	Methyl alcohol	Phosphates	II.	3	114
Acetic anhydride	Acetic acid	Phosphates	IV.	1	384
"	Acetylene and acetic acid.	Mercury salts	IV.	1	373
Acetone	Acetic acid	BaCO <sub>3</sub> ; CaO; Al <sub>2</sub> O <sub>3</sub> ; etc.	II. IV.	10 1	259 259
"	Alcohol or acetylene and steam.	Iron-alkali.	II.	10	260
"	Carbohydrates	Fermentation	III.	4	349
Acetylsalicylic acid.	Salicylic acid	Anhydrous sodium acetate. Sulphuric acid.	IV.	3	412.
Aliphatic amines	Alcohol and ammonia.	Alumina	II.	10	257
Alkyl benzenes	Olefines and benzene.	AlCl <sub>3</sub> ; H <sub>2</sub> SO <sub>4</sub> ; phosphoric acid.	IV.	4	433
Amyl acetate	Amyl alcohol and acetic acid.	Sulphuric acid	IV.	3	410
Amyl salicylate	Amyl alcohol and salicylic acid.	" "	IV.	3	410
Aniline	Chlorobenzene and ammonia.	Copper and copper salts.	IV.	4	436
"	Nitrobenzene	Copper	II.	11	307
Aniline black	Aniline	Vanadium and osmium compounds	IV.	4	441
Anthraquinone (via o-benzoyl benzoic acid).	Benzene and phthalic anhydride.	Aluminium chloride.	IV.	4	431
Anthraquinone	Anthracene	Vanadium oxide.	II.	10	263
Anthraquinone sulphonic acids	Anthraquinone	Mercuric sulphate	IV.	4	442
Aromatic aldehydes.	Hydrocarbons and CO or HCN.	Aluminium and cuprous chlorides	IV.	4	434
Aromatic halides	Diazo-compounds	Cuprous salts; copper.	IV.	4	435
Aromatic hydrocarbons.	Sulphonic acids	Mercury salts	IV.	4	442
Aromatic thio-compounds.	Various	Iodide; copper salts.	IV.	4	442
Benzal chloride	Toluene	PCl <sub>5</sub> ; S <sub>2</sub> Cl <sub>2</sub>	IV.	4	437
Benzaldehyde	Chlorinated toluene.	Iron salts	IV.	2	404
"	Toluene	Ceric or ferric sulphates.	IV.	4	441
"	"	Vanadium oxide.	II.	10	263
Benzanthraquinone (via α-naphthoyl benzoic acid).	Naphthalene and phthalic anhydride.	Aluminium chloride.	IV.	4	431
Benzene sulphonic acids.	Benzene	Iodine; hydriodic acid.	IV.	4	442
Benzotrifluoride	Benzotrifluoride.	Iron salts and alkali.	IV.	2	404

# xiv CLASSIFIED LIST OF PRODUCTS

Product.	From.	Catalyst.	Sect.	Chap.	Page.
Benzoic acid	Toluene	Vanadium oxide.	II.	10	263
Benzotrichloride.	Toluene	$PCl_3$ ; $S_2Cl_2$	IV.	4	437
Benzyl acetate	Benzyl alcohol and acetic acid.	Sulphuric acid	IV.	3	410
Benzyl benzoate.	Benzaldehyde	Sodium	IV.	3	408
Benzyl chloride	Toluene	$PCl_3$ ; $S_2Cl_2$	IV.	4	437
Bornyl acetate	Borneol and acetic acid.	Sulphuric acid	IV.	3	410
n-Butyl alcohol	Carbohydrates	Fermentation	III.	4	349
" "	Crotonaldehyde	Nickel	(IV.) II.	1	380
Butyl aldehyde	Butyl alcohol	Copper	II.	10	249
Butylene	n-Butyl alcohol	Alumina	II.	10	257
Butyric acid	Carbohydrates	Fermentation	III.	2	339
Camphor	Borneol	Copper	II.	10	250
Carbanilides	Aniline and carbon dioxide.	Aluminium chloride.	IV.	4	432
o-Carboxyphenyl glycine.	o-Chlorbenzoic acid and glycine.	Copper	IV.	4	435
Cellulose acetates	Cellulose	Sulphuric acid, zinc chloride, etc.	IV.	3	412
Chloracetic acid.	Acetic acid	Sulphur	IV.	4	438
Chlorobenzenes.	Benzene	Iron chloride	IV.	4	437
Citric acid.	Carbohydrates	Fermentation	III.	2	341
Crotonaldehyde	Acetaldehyde	Alkalies	IV.	1	379
Crystal violet	Dimethylaniline and $COCl_2$ .	Aluminium chloride.	IV.	4	432
Cyclohexanols	Phenols	Nickel	II.	11	296
Cyclohexanones	Cyclohexanols	Copper	II.	10	250
Decahydronaphthalene (decalin).	Naphthalene	Nickel	II.	11	298
4,4'-Dihydroxybenzophenone.	Phenol and carbon dioxide.	Aluminium chloride.	IV.	4	432
p-Dimethylamino-benzoic acid.	Dimethylaniline and carbon dioxide.	Zinc chloride	IV.	4	432
Diphenyl ether	Phenol	Alumina, thoria, etc.	II.	10	257
" "	Phenol and carbon dioxide.	Aluminium chloride.	IV.	4	432
Ether	Alcohol	Sulphuric acid	IV.	3	414
Ethyl acetate	Acetaldehyde	Aluminium ethylate.	IV.	1	378
" "	Alcohol and acetic acid.	Sulphuric acid	IV.	3	409
" "	Ethyl alcohol	Copper-alumina; copper-chromium oxide.	IV.	1	379
Ethyl alcohol	Acetaldehyde	Nickel	(II.) IV.	10	250
" "	Cellulose	Fermentation	III.	4	356

# CLASSIFIED LIST OF PRODUCTS

xv

Product.	From.	Catalyst.	Seal.	Chap.	Page.
Ethyl alcohol	Cellulose	Mineral acids, followed by fermentation.	IV.	2	397
" "	Ethylene	Sulphuric acid.	IV.	1	387
" "	Ethylene and steam.	Alumina, thorfa.	IV.	1	390
" "	Starch	Mineral acids, followed by fermentation.	IV.	2	395
" "	Sugar	Fermentation	III.	1	324
Ethyl benzoate	Ethyl alcohol and benzoic acid.	Sulphuric acid	IV.	3	410
Ethyl cinnamate.	Ethyl alcohol and cinnamic acid.	Hydrogen chloride	IV.	3	411
Ethyl citrate	Ethyl alcohol and citric acid.	" "	IV.	3	410
Ethylene	Alcohol	Alumina, thorfa, etc.	II.	10	254
"	"	Sulphuric, phosphoric acid.	IV.	3	417
Ethylidene diacetate.	Acetylene and acetic acid.	Mercury salts	IV.	1	373
Ethyl lactate	Ethyl alcohol and lactic acid.	Hydrogen chloride.	IV.	3	410
Ethyl succinate	Ethyl alcohol and succinic acid.	Sulphuric acid	IV.	3	410
Fatty acids	Fats	Fermentation	III.	5	362
" "	"	CuO, MgO ; Twitchell agent.	IV.	2	400
Formaldehyde	Hydrocarbons	Metallic oxides	II.	10	263
"	Methyl alcohol	Copper	II.	10	241
Geranyl acetate	Geraniol	Anhydrous sodium acetate.	IV.	3	411
Gluconic acid	Glucose	Fermentation	III.	2	342
Glucose	Starch	Mineral acids	IV.	1	395
Glycerine	Sugar	Fermentation	III.	1	332
Glycol ethers	Ethylene oxide ; ethylene chlorhydrin.	Fuller's earth	IV.	3	418
n-Heptyl alcohol	Ethylene oxide, and n-pentane.	Aluminium chloride.	IV.	4	434
Hexachlorethane	Ethyl chloride	Charcoal	II.	12	317
Hexalin (Sextol).	Phenol	Nickel	II.	11	296
Higher alcohols	Water-gas	Zinc chromates, etc.	II.	3	110
Higher fatty alcohols.	Fats and fatty oils	Copper chromate	II.	11	292
Humins, etc.	Waste cellulose and plant matter.	Fermentation	III.	4	359
Hydrocarbons (motor spirit).	Coal, tars, etc.	Iron, tin compounds, oxides and sulphides of molybdenum and tungsten?	II.	4	134

# xvi CLASSIFIED LIST OF PRODUCTS

Product.	From.	Catalyst.	Sect.	Chap.	Page.
Hydrocarbons (motor spirit)	Fats and fatty oils	Nickel ; chlorides or oxides of Cu, Mg, etc.	II.	11	294
" " "	Gaseous olefines.	Phosphoric acids.	IV.	5	457
" " "	Phenols	MoO <sub>3</sub> ; MoS <sub>2</sub>	II.	4	130
" " "	Water-gas	Cobalt-thorium oxide.	II.	3	115
Hydrogenated (hardened) fats	Natural liquid fats.	Nickel (palladium, etc.).	II.	11	276
Hydrogen sulphide.	Carbon disulphide	Nickel	II.	9	237
β-Hydroxyethyl-naphthalenes	Ethylene oxide and naphthalene.	Aluminium chloride.	IV.	4	434
β-Hydroxyethyl-pyridines.	Ethylene oxide and pyridine.	" "	IV.	4	434
Indigo	o-Nitrobenzaldehyde and acetone.	Sodium hydroxide	IV.	4	423
Ionone	Citral and acetone	Baryta, etc.	IV.	4	422
Lactic acid	Carbohydrates	Fermentation	III.	2	338
Linalyl acetate	Linalool	Anhydrous sodium acetate.	IV.	3	411
Lubricating oils	Olefines	Aluminium chloride ; boron trifluoride.	IV.	5	456
Maleic and malic acids.	Benzene	Vanadium oxide	II.	10	263
Menthol	Thymol ; piperitone.	Nickel	II.	11	301
Menthyl acetate	Menthol	Anhydrous sodium acetate.	IV.	3	411
Methane	Water-gas	Nickel, etc. ; MoS <sub>2</sub>	II.	3	97
Methylal	Formaldehyde	Hydrogen chloride	IV.	3	414
Methyl alcohol	Water-gas	Zinc chromates, etc.	II.	3	105
Methyl anthranilate.	Methyl alcohol and anthranilic acid.	Hydrogen chloride	IV.	3	411
Methyl benzoate	Methyl alcohol and benzoic acid.	Sulphuric acid	IV.	3	410
Methyl cinnamate	Methyl alcohol and cinnamic acid.	Hydrogen chloride	IV.	3	411
Methylethyl ketone.	iso-Butyl alcohol.	Copper	II.	10	249
Methyl hexalins.	Cresols	Nickel	II.	11	296
Methyl salicylate	Methyl alcohol and salicylic acid.	Sulphuric acid	IV.	3	410
Michler's ketone	Dimethylaniline and carbon dioxide.	Aluminium chloride.	IV.	4	432
Nitraniline derivatives.	Chloro-nitro-compounds and ammonia.	Copper	IV.	4	435
Oxidised (dried) fatty oils.	Drying oils	Oxides or salts of Pb, Mn, Co.	IV.	4	440

# CLASSIFIED LIST OF PRODUCTS xvii

Product.	From.	Catalyst.	Sect.	Chap.	Page.
Palmitone . . .	Palmitic acid . .	$Al_2O_3$ ; $SiO_2$ ; $FeO$ .	II.	10	260
Paraldehyde . .	Acetaldehyde . .	Hydrogen chloride.	IV.	1	377
Phenol . . .	Chlorobenzene and alkalis.	Copper or copper salts.	IV.	4	436
Phenol-aldehyde resins.	Phenols and formaldehyde (other aldehydes).	Alkalies ; acids .	IV.	1, 4	377, 424
Phenylethyl alcohol.	Ethylene oxide and benzene.	Aluminium chloride.	IV.	4	434
Phthalic anhydride	Naphthalene . .	Mercuric sulphate	IV.	4	441
" " "	" " "	Vanadium oxide	II.	10	263
Piperidines . .	Pyridines . . .	Nickel . . .	II.	11	300
iso-Propyl alcohol	Acetone . . .	Nickel . . .	II.	10	252
Quinone . . .	Benzene . . .	Vanadium oxide	II.	10	263
Resins (polymer)	Coumarone, styrene, vinyl acetate, etc.	Sulphuric acid ; alkali metals, etc.	IV.	5	454
Rubber substitutes.	Isoprene, etc. .	Sodium ; oxidising agents, etc.	IV.	5	451
Salicylic acid . .	Phenol and carbon dioxide.	Aluminium chloride.	IV.	4	432
Stearone . . .	Stearic acid . .	$Al_2O_3$ ; $SiO_2$ ; $FeO$ .	II.	10	260
Sulphur . . .	Alkali waste . .	Iron oxide . .	II.	9	232
Tetrachlorethane	Acetylene . . .	$SbCl_5$ . . .	IV.	4	439
Tetrahydro-naphthalene ) (tetralin). )	Naphthalene . .	Nickel ; $MoS_2$ .	II.	11	298, 300
Toluene . . .	Benzene . . .	Aluminium chloride.	IV.	4	431
Urea . . .	Ammonia and carbon dioxide.	—	II.	5	171
Urea-aldehyde resins.	Urea and formaldehyde.	Alkalies ; acids .	IV.	4	427
Vinyl acetate . .	Acetylene . . .	Mercury salts . .	IV.	1	373
Vulcanised rubber	Rubber and sulphur.	Organic bases ; various organic nitrogen and sulphur compounds.	IV.	4	443

# CLASSIFIED LIST OF CATALYSTS DEALT WITH IN SECTIONS II TO IV

Catalyst.	Process.	Sect.	Chap.	Page.
Acids (mineral)	Condensation reactions :—			
„ „	Production of acetals . . . .	IV.	3	414
„ „	„ „ ionone . . . .	IV.	4	422
„ „	„ „ phenol-aldehyde resins	IV.	4	424
„ „	„ „ polymer resins . . . .	IV.	5	454
„ „	„ „ urea-aldehyde resins . .	IV.	2	427
„ „	Hydrolysis of cellulose . . . .	IV.	2	397
„ „	„ „ starch . . . .	IV.	2	395
Alkalies	Condensation reactions :—			
„ „	Production of ionone . . . .	IV.	4	422
„ „	„ „ phenol-aldehyde resins	IV.	4	424
„ „	„ „ urea-aldehyde resins . .	IV.	4	427
Alkali halides	Production of cyanamide . . . .	II.	5	170
Alkali metals	„ „ „ polymer resins . . . .	IV.	5	454
Alumina	Dehydration of alcohols . . . .	II.	10	254
„ „	Diphenyl ether from phenol . .	II.	10	257
„ „	Ethyl acetate from ethyl alcohol	IV.	1	379
„ „	Ethyl alcohol from ethylene and steam	IV.	1	390
„ „	Hydrogen from hydrocarbons . .	II.	2	90
„ „	Hydrogen cyanide from ammonia .	II.	5	174
„ „	Ketones from fatty acids . . . .	II.	10	259
Aluminium chloride.	Friedel and Crafts reaction . .	IV.	4	431— 434
„ „	Polymerisation : lubricating oils from olefines.	IV.	5	456
Aluminium ethy- late.	Ethyl acetate from acetaldehyde .	IV.	1	378
Antimony penta- chloride.	Chlorination of acetylene . . .	IV.	4	439
Barium carbonate	Ketones from organic acids . . .	II.	10	258
Baryta . . . .	Condensation of citral and acetone (ionone).	IV.	4	422
Bases (organic)	Vulcanisation of rubber . . . .	IV.	4	413
Bismuth oxide	Oxidation of ammonia . . . .	II.	6	186
Boron trifluoride.	Polymerisation : lubricating oils from olefines.	IV.	5	456
Calcium carbonate	Ketones from organic acids . . .	II.	10	259
Calcium chloride	Hydrogenation-cracking of fatty oils (motor spirit production).	II.	11	294
„ „	Production of acetals . . . .	IV.	3	414
„ „	„ „ „ cyanamide . . . .	II.	5	170
Calcium oxide	Hydrogenation-cracking of fatty oils (motor spirit production).	II.	11	294
„ „	Hydrolysis of fats . . . .	IV.	2	400



# CLASSIFIED LIST OF CATALYSTS xix

Catalyst.	Process.	Sect.	Chap.	Page.
Ceric sulphate	Oxidation of toluene	IV.	4	441
Cerium oxide	" " carbon monoxide to carbon dioxide.	II.	3	104
" "	" " ammonia	II.	6	186
Charcoal	Chlorination of ethyl chloride	II.	12	317
"	Synthesis of carbonyl chloride	II.	12	315
"	" " hydrochloric acid	II.	12	316
"	" " sulphuryl chloride	II.	12	316
Chromium oxide.	Ammonia oxidation	II.	6	186
" "	Ethyl acetate from ethyl alcohol	IV.	1	379
" "	Higher alcohols from water-gas	II.	3	110
" "	Methyl alcohol from water-gas	II.	3	105
" "	Oxidation of carbon monoxide to carbon dioxide.	II.	3	104
Cobalt oxide	Drying (oxidation) of vegetable oils	IV.	4	440
Cobalt salts	" " " " " "	IV.	4	440
Cobalt-thoria	Hydrocarbons (motor spirit) from water-gas.	II.	3	115
Copper	Dehydrogenation of aldehydes and ketones.	II.	10	245
"	Ethyl acetate from ethyl alcohol	IV.	1	379
"	Gattermann reaction	IV.	4	434
"	Oxidation of alcohol	II.	10	241
"	Production of aromatic thio-compounds.	IV.	4	442
"	Reduction of nitrobenzene	II.	11	307
"	Sandmeyer reaction	IV.	4	435
Copper chlorides	Chlorination of paraffins	IV.	4	438
"	Gattermann reaction	IV.	4	434
"	Production of chlorine (Deacon-Hurter).	II.	8	220
Copper chromate	Higher alcohols from fats	II.	11	292
Copper oxide	Ammonia oxidation	II.	6	186
" "	Oxidation of carbon monoxide to carbon dioxide.	II.	3	104
Copper phosphate	Acetic acid from water-gas	II.	3	114
Copper salts	Gattermann reaction	IV.	4	434
" "	Production of aromatic thio-compounds.	IV.	4	442
" "	Sandmeyer reaction	IV.	4	435
Enzyme catalysts.	Fermentation Processes	III.		
(Note.—With the exception of the enzyme "lipase," the following represent the organisms which produce the enzyme or enzymes forming the catalytic agent.)				
<i>Aspergillus niger</i>	Gluconic acid from glucose	III.	2	342
<i>Bacterium aceti</i>	Acetic acid from alcohol	III.	3	343
<i>Bacterium aceti lacti.</i>	Lactic acid from sugar and starch	III.	2	338
<i>Bacterium butyricus.</i>	Butyric acid from sugar or starch	III.	2	339
<i>Bacterium xylinus.</i>	Acetic acid from alcohol	III.	3	343



# CLASSIFIED LIST OF CATALYSTS xxi

Catalyst.	Process.	Sect.	Chap.	Page.
Magnesium oxy-chloride.	Chlorine manufacture (Weldon-Péchiney).	II.	8.	228
Manganese acetate	Acetic acid from acetaldehyde .	IV.	1	381
Manganese oxide	Chlorine manufacture (Weldon process).	II.	8	229
" "	Higher alcohols from water-gas .	II.	3	110
" "	Oxidation (drying) of vegetable oils .	IV.	4	440
" "	Oxidation of carbon monoxide to carbon dioxide.	II.	3	104
" "	Oxidation of toluene .	IV.	4	441
Manganese salts .	Oxidation (drying) of vegetable oils .	IV.	4	440
Mercury salts .	Acetic anhydride from acetylene and acetic acid.	IV.	1	373
" "	Aromatic hydrocarbons from sulphonic acids.	IV.	4	442
" "	Ethylidene diacetate from acetylene .	IV.	1	373
" "	Vinyl acetate from acetylene .	IV.	1	373
Mercury sulphate	Oxidation of naphthalene to phthalic anhydride.	IV.	4	441
" "	Sulphonation of aromatic compounds .	IV.	4	442
Molybdenum oxide	De-oxygenation of phenols .	II.	4	130
" "	Hydrogenation-cracking of coal, tars, etc.	II.	4	134
Molybdenum sulphide.	" " " "	II.	4	134
" "	Hydrogenation of naphthalene .	II.	4	131
" "	" " " "	II.	11	300
" "	Methane from water-gas .	II.	3	100
Nickel .	Hydrogen from hydrocarbons .	II.	2	90
" "	Hydrogenation of aldehydes and ketones.	II.	10	250
" "	" " " "	IV.	1	380
" "	Hydrogenation of aromatic and terpene compounds.	II.	11	295
" "	Hydrogenation of fats .	II.	11	276
" "	Hydrogenation-cracking of fatty oils (motor spirit production).	II.	11	294
" "	Production of methane from water-gas .	II.	3	97
" "	Removal of carbon disulphide from coal gas.	II.	9	237
Nitrogen oxides .	Sulphuric acid (chamber process) .	II.	7	211
Osmium compounds.	Aniline black from aniline .	IV.	4	441
Palladium .	Hydrogenation of fats .	II.	11	276
Peroxides .	Polymerisation : synthetic resins .	IV.	5	455
" "	" " synthetic rubber .	IV.	5	451
Phosphates .	Acetic acid from methyl alcohol .	II.	3	114
" "	Acetic anhydride from acetic acid .	IV.	1	384
" "	Ethyl alcohol from ethylene and steam .	IV.	1	390
Phosphoric acids.	Acetic anhydride from acetic acid .	IV.	1	384
" "	Alkyl benzenes from olefines and benzene.	IV.	4	433
" "	" " " "	"	"	"
" "	Ethylene from alcohol .	IV.	3	417
" "	Polymerisation of gaseous olefines (" polymer petrol ").	IV.	5	457

# xxii CLASSIFIED LIST OF CATALYSTS

Catalyst.	Process.	Sect. Chap.	Page.
Phosphorus	Chlorination of acetic acid	IV.	438
Phosphorus tri-chloride.	Chlorination of hydrocarbons	IV.	437
Platinum	Hydrogenation of fats	II.	276
	Oxidation of ammonia	II.	181
	Sulphuric acid (contact process)	II.	203
Rubidium oxide	Higher alcohols from water-gas	II.	110
Silica	Dehydration of alcohols	II.	254
"	Ketones from organic acids	II.	258
Sodium	Benzyl benzoate from benzaldehyde	IV. 3	408
"	Polymerisation : synthetic rubber	IV. 5	451
Sodium acetate	Acetylation with acetic anhydride	IV. 3	411
Sodium hydroxide	Condensation of <i>o</i> -nitrobenzaldehyde and acetone (indigo).	IV. 4	423
Sulphur	Chlorination of acetic acid	IV. 4	438
Sulphur dichloride	Chlorination of hydrocarbons	IV. 4	437
Sulphuric acid	Acetylation with acetic anhydride	IV. 3	412
" "	Alcohols from olefines	IV. 1	387
" "	Dehydration of alcohols (ethers)	IV. 3	414
" "	" " (olefines)	IV. 3	417
" "	Esterification of alcohols by organic acids.	IV. 3	409
" "	Hydrolysis of fats	IV. 2	403
" "	Polymerisation : synthetic resins	IV. 5	454
Thoria	Dehydration of alcohols	II. 10	254
"	Ethyl alcohol from ethylene and steam	IV.	390
"	Hydrocarbons (motor spirit) from water-gas.	II.	115
"	Hydrogen cyanide from ammonia, etc.	II. 5	174
Tin compounds	Hydrogenation-cracking of coals	II. 4	134
" " oxide	" " " fatty oils	II. 11	294
" " "	" " " tars, oils, etc.	II. 4	134
" " "	Oxidation of ammonia	II. 6	186
Tungsten sulphide	Hydrogenation-cracking of tars, oils, etc.	II. 4	134
Twitchell agent	Hydrolysis of fats	IV. 2	402
Vanadium compounds.	Aniline black from aniline	IV. 4	441
Vanadium pent-oxide.	Oxidation of aromatic hydrocarbons, benzene, naphthalene, anthracene, etc.	II.	263
" " "	Sulphuric acid (contact process)	II. 7	203
Zinc chloride	Acetylation with acetic anhydride	IV. 3	412
" " "	Friedel and Crafts reaction	IV. 4	431
Zinc chromates	Higher alcohols from water-gas	II. 3	110
" " "	Methyl alcohol from water-gas	II. 3	105
Zinc oxide	Hydrogenation-cracking of fatty oils (motor spirit production).	II. 11	294
" " "	Hydrolysis of fats	IV. 2	400
Zirconia	Hydrogen cyanide from ammonia, etc.	II. 5	174

# CATALYTIC PROCESSES IN APPLIED CHEMISTRY

## SECTION I

### CHAPTER I

#### GENERAL DEVELOPMENT OF THE USE AND UNDERSTANDING OF CATALYTIC PROCESSES

ALTHOUGH catalytic changes were first so called by Berzelius<sup>1</sup> about the year 1835, they were recognised much earlier, and some of them were used in preparing chemical products several centuries before that date. Since, as we shall see, fermentation is also a case of catalytic action, it is obvious that catalysis has played an important (if unrecognised) part from the earliest times in the production of alcoholic liquors, and also of vinegar and some other simple commodities of this type. Of products which are more definitely in the category of "chemicals," the preparation of ether by the action of sulphuric acid on alcohol was familiar to the alchemists; sulphuric acid itself was made by the alchemists by combustion of a mixture of sulphur and nitre, and about 1740 Roebuck and others introduced the chamber process for manufacturing sulphuric acid, in which large amounts of sulphur dioxide were oxidised to sulphuric acid by the use of comparatively small proportions of oxides of nitrogen. At the commencement of the nineteenth century Clément and Désormes<sup>2</sup> and Sir Humphry Davy investigated the mechanism of this oxidation process, and showed in fact that the oxides of nitrogen had the functions of what we now term a catalyst.

Davy<sup>3</sup> also noticed a number of interesting chemical changes which were induced by the presence of heated platinum wire or sponge, such as the union of oxygen with hydrogen, volatile hydrocarbons, or alcohol. This marks one of the first scientific investigations in the realm of what is now known as heterogeneous catalysis, or catalysis at the surfaces of solids. He, with subsequent workers, also appreciated the poisoning or inhibiting action on the platinum of certain gases such as hydrogen sulphide and other gaseous sulphur compounds, ammonia, etc.

Somewhat later, but still prior to the Berzelian nomenclature of catalysis, Faraday<sup>4</sup> extended Davy's observations on platinum, developing with characteristic genius views, substantially unmodified even at the present day, upon the mechanism of contact action and the requisites for maintaining full activity in the contact material. Thus, in dealing with the ability of platinum to effect the union of hydrogen and oxygen, he sums up the practical points of the contact agent in the following sentence: "The only essential condition appears to be a perfectly clean and metallic surface, for whenever that is present the platina acts, whatever its form and condition in other respects may be; and though variations in the latter points will very much affect the rapidity, and therefore the visible appearances and secondary effects of the action, that is, the ignition of the metal and the inflammation of the gases, they, even in their most favourable state, cannot produce any effect unless the condition of a clean, pure, metallic surface be also fulfilled."

He also expresses a general opinion as to the mechanism of these actions, which must be recognised as extraordinarily close in its main outlines to present-day views on the subject, namely, that catalytic action is conditioned by preliminary adsorption or incipient chemical combination between the interacting materials and a third agent (the catalyst): "All the phenomena connected with this subject press upon my mind the

conviction that the effects in question are entirely incidental and of a secondary nature ; that they are dependent upon the natural conditions of gaseous elasticity combined with the exertion of that attractive force possessed by many bodies, especially those which are solid, in an eminent degree, and probably belonging to all ; by which they are drawn into association more or less close, without at the same time undergoing chemical combination though often assuming the condition of adhesion ; and which occasionally leads, under very favourable circumstances, as in the present instance, to the combination of bodies simultaneously subjected to this attraction. I am myself prepared to admit (and probably many others are of the same opinion), both with respect to the attraction of aggregation and of chemical affinity, that the sphere of action of particles extends beyond those other particles with which they are immediately and evidently in union, and in many cases produces effects rising into considerable importance."

So that Faraday, who formulated these conclusions in 1833-1834, had clearly established in his own mind the general causes and effects of what is now termed heterogeneous catalysis.

As already stated, in 1835 Berzelius<sup>1</sup> surveying a number of chemical changes, the mechanism of which appeared difficult to understand in the light of then current explanations, suggested that such processes, which in many cases apparently proceeded in the presence of a specific agent but not in its absence, were due to the operation of what he called a catalytic force. He termed the particular agents which exhibited this force "catalysts," and held that the force in question was in some way a novel form or manifestation of chemical affinity. A few years later Liebig, discussing similar processes more or less from the standpoint of ferment action, put forward his vibration theory of catalysis, according to which a catalyst was simply in a state of molecular vibration which happened to

synchronise with, or at any rate be capable of communication to, other molecules, with the result that the latter were, so to speak, shaken to pieces, or in other words suffered decomposition. This vibration hypothesis did not survive the test of experiment and observation, whilst the catalytic force theory of Berzelius in its original form is more remote from the present-day conception of what goes on in catalytic action than Faraday's simple statement quoted above.

The academic classification and consideration of catalysis during the nineteenth century was somewhat confused, and may perhaps be passed over in the present book until we come to the modern theories as enunciated by Ostwald,<sup>5</sup> H. E. Armstrong,<sup>6</sup> and many others. These, to which we shall return a little later, were formerly of two distinct types, namely, those which relied on purely physical factors, and those which involved the assumption of the intermediate formation of something akin to definite chemical compounds; of late years these somewhat divergent views have more or less been reconciled or synthesised into the present adsorption or unstable intermediate-compound theory of the mechanism of catalysis.

We will revert for the moment, however, to what is the more immediate concern of this book, namely the development of the use of catalytic processes in industry during the past 150 years.

It is well, in view of the great advances which have been made in recent years in the theoretical understanding of catalysis, to get the facts concerning its industrial applications in approximately correct perspective. Dozens of catalytic processes were brought into use during the nineteenth century, some by pure empiricism, others by a combination of practical trials with such small fundamental knowledge as was then available, but in almost all these cases the inspiration may fairly be attributed to chemical intuition rather than to theoretical deduction.\* As in many other fields of applied physical chemistry, fundamental theory



until recent years lagged far behind practical applications; and it is fair to enumerate some of the many instances in which contact action was successfully utilised on a technical scale without the advantage of the guidance of the laws of thermodynamics or, for example, of Ostwald's so-called criteria of catalysis. Thus, the production of sulphuric acid by passage of air and sulphur dioxide over platinum was patented in 1831, and the similar oxidation of ammonia to nitric acid was discovered in 1839, although it is true that in these cases efficient technical use of the methods had to await further information concerning the phenomenon of catalyst poisoning. On the other hand, the three processes of Weldon, Deacon and Weldon-Péchiney for the manufacture of chlorine were successfully worked out and practised on a very large scale from about 1860-1870 onwards, and in quite another direction the purification of coal gas from hydrogen sulphide by passage over iron oxide (which is essentially catalytic in nature), and the use of the Claus kiln in the Chance recovery process for the recovery of sulphur from alkali waste, have been carried on for very many years.

Turning to applied organic chemistry, the production of ether from alcohol by sulphuric acid was, it is true, made the subject of theoretical study by Williamson, Berthelot, and others, but in many other cases catalytic action was (and is) carried out on a technical scale more or less independently of theoretical considerations. It is only necessary to instance the manufacture of formaldehyde by passage of methyl alcohol and air over heated copper, the production of acetone by passage of acetic acid vapour over heated chalk, the many processes in which mineral acids are used to effect the addition of water to materials such as the more complex carbohydrates or the esters, and also to effect esterification of alcohols, or the use of metallic oxides in the autoclave processes for the hydrolysis of fats, to realise the large extent to which processes of

the more or less conventional catalytic type have been developed.

The variety of catalytic actions employed in the organic chemical industries, in cases which have not even yet been systematically studied from a fundamental point of view, is still more striking. The methods to which we refer are those used in a wide variety of technical syntheses of coal-tar products, such as the employment of many different chlorinating agents and sulphonating agents, and the use of numerous specific compounds to effect condensation of organic molecules, usually with elimination of the elements of water, hydrogen chloride, etc. In the latter category may be mentioned such compounds as aluminium chloride, sodium, alkaline hydroxides or ethoxides, etc., anhydrous or aqueous solutions of mineral acids of varying concentrations, and, for example, the use of sodium acetate or zinc chloride as an aid to acetylation.

The above statement is intended not so much to belaud empiricism (although the technical results obtained in spite of lack of theoretical guidance merit commendation) as to indicate the need for systematic academic study of these less understood examples of industrial catalysis; for it is not unreasonable to predict that treatment of these methods on similar lines to those which have been so successfully applied to, for example, the modern synthetic ammonia, methyl alcohol, and other industries could not fail to be eminently fruitful.

Coming to the main advantages of the use of catalysts in technical methods, and without precisely defining the term "catalyst" until a little later, it is evident that the chief object to be gained is the elimination of the use of accessory chemicals. Since the latter react in equivalent proportions, it is, of course, obvious that, in addition to their consumption in amounts corresponding to the output of the desired product, there is also the concurrent formation of an equivalent amount

of by-products which, very frequently are of little value, or at least require considerable further treatment before they acquire an adequate market value. Under ideal conditions (and it may be borne in mind that the ideal is often quite reasonably approachable) a catalyst can often be found which will induce a desired chemical reaction with the formation of very few by-products of a useless nature, and which is capable of effecting the transformation of many times its own weight of interacting material.

The actual amount so transformed in practice varies widely. In some of the organic chemical processes in which the catalyst itself is apt to become altered by side reactions, the amount may only be of the order of say 50–100 times the weight of catalyst present; at the other extreme we have instances such as the use of platinum gauze in the oxidation of ammonia, where with suitable precautions the life of the catalyst is practically indefinite and the rate of transformation exceedingly great (thus a piece of platinum gauze 6 in. by 4 in. is capable of producing about 12 lb. of nitric acid per hour). Broadly speaking, then, the first economic objective of a technical catalytic process is the elimination, or reduction to a minimum, of the use of accessory chemicals.

There is another aspect to be considered, namely, the economy of energy as well as of material. The conventional forms of catalyst sometimes lead to economy in both directions—that is to say, whilst avoiding the use of additional chemicals a reaction may also be carried out at, for example, a much lower temperature than would be possible in the absence of a catalyst, or a process may become possible which, in the absence of a catalyst, requires the application of considerable actinic (photo-chemical) or electrical energy; etc. On the other hand, many of the modern processes of catalysis involve the use of very high pressures and, in some cases, high temperatures—in other words, the consumption of considerable energy

in the form of power and heat. Many of the latter type are proving very successful in technical practice, but this should not entirely blind us to the fact that we have at command a whole range of natural catalysts which operate at or close to the ordinary temperature, in some cases with exceedingly great efficiency, if we only knew how to use them.

The investigation and utilisation of the enzymes produced by living organisms is a field of industrial research which, up to the present, has received little systematic investigation. It is, of course, impossible to expect that anything but a proportion of the variety of chemical products required by modern civilisation can be prepared by processes of the nature of fermentation; but it is equally certain that far more use could be made of enzyme action in industry in many directions, for enzyme action is often closely connected with hydrolysis and also with the reverse action of condensation or dehydration, and it is further capable, in specific cases, of effecting oxidation or reduction; the elaboration of nitrogen compounds by enzyme action is another region in which there obviously may be possibilities. As already stated, enzyme actions proceed under the ordinary conditions of temperature and pressure, and the prospect, even if remote, of combining economy in fuel costs with that of accessory chemicals is sufficiently attractive to invite more intensive study of this field.

For these reasons, certain processes of fermentation or enzyme action which are already in use for the production of specific chemical products have been treated in appropriate sequence in this book as instances of applied catalysis. The examples at present available (with the exception of alcohol, acetic and lactic acids, acetone and butyl alcohol) are neither numerous nor, perhaps, relatively important; it is, however, well to stress the point that these processes are fundamentally of the same nature as the more ordinary forms of catalytic action, and, although the biochemical

technique involved is of course quite different in many aspects from the manipulation necessary in the cases of ordinary chemical contact agents, the fundamental action in both cases is at present understood to be of the same nature. Thus, from both a theoretical and a practical point of view, it is most desirable to bring fermentation processes into line with the more conventional technical catalytic methods.

We may now return to a brief survey of the general development of theoretical views of catalytic action during the past thirty to forty years. In the first place we may refer to the restatement of the earlier views of Berzelius, Liebig, etc., on catalysis by Ostwald in 1888; he laid down a series of "criteria" of catalysis, the most important of which was the definition that "catalysts are substances which change the velocity of a given chemical reaction without modification of the energy factors of the reaction."

It is by no means agreed, however, that a catalyst can only alter the speed of a chemical reaction which would take place (possibly exceedingly slowly) in any case; the view has been maintained consistently by various workers throughout the development of catalytic theory that a catalyst can actually initiate a chemical change, that is to say, can cause an action to occur which in its absence would definitely not proceed. (Of course, this case can be included in Ostwald's criteria by saying that such chemical changes proceed only at infinitely slow speeds in the absence of a catalyst; but this is tantamount, for all practical purposes, to accepting the statement that a catalyst can cause a chemical change to take place which otherwise would not occur.)

At the same time it is equally clear that no catalyst can operate against the fundamental laws of thermodynamics. The present knowledge of the application of these laws enables, in many cases, data as to the equilibria or thermal conditions of chemical changes to be determined from a perfectly general point of view;

and, if the appropriate physical and chemical constants of the particular interacting compounds which are required in these calculations are known with sufficient accuracy, it becomes possible to state whether a given chemical reaction is thermodynamically possible or not, quite independently of the intervention of any catalyst. Given energy conditions which allow a certain reaction to take place, two cases arise: the action may not proceed with measurable speed in the absence of a catalyst, or it may take place at any particular rate. In either case the presence of appropriate compounds may cause a marked alteration in the progress of the reaction in question; it may cause the change to proceed at a useful speed where otherwise it could not be carried out at all, it may accelerate a slow reaction, or, on the other hand, it may induce a retardation of the normal rate of action ("negative catalysis").

From the point of view of the technologist it seems more useful to define a catalyst as a substance which alters the speed of reaction (including the case of apparent initiation of reaction), but which remains unaltered in chemical composition after the chemical change is completed. This definition covers a number of cases which we shall encounter in which the physical state of the catalyst may undergo alteration as the main reaction proceeds, whilst it also emphasises the important factor that, if the catalyst itself is chemically changed by side-reactions (catalyst poisoning), it is no longer able to function as a catalyst and the main reaction tends to revert towards its normal, non-catalysed rate of progress.

Catalytic action is at present recognised, so far as chemical affinity is concerned, to proceed in accordance with the same natural laws which operate in any other chemical change. The energy changes taking place in a catalysed system, and the way in which the catalyst transfers, or continuously acquires, the energy necessary to enable the chemical change to proceed, are not so clearly defined at present as the purely chemical side

of the question ; but, on the other hand, this state of affairs is not peculiar to catalysis, for our lack of understanding of the precise energy relations during chemical change extends to a large number of reactions of many kinds.

Chemically speaking, catalytic changes proceed, as already stated, according to the laws of thermodynamics, and consequently follow the general principles of chemical kinetics and of the law of mass action ; but, as will be explained in the next chapter, it is necessary to have an explicit knowledge of the local conditions in a catalytic system in order to understand the specific application of the law of mass action in particular cases.

The modern developments of catalytic theory are the result of a very large quantity of experimental observations which have been carried out by numerous groups of workers in many countries ; they have undoubtedly led to the elucidation of much that was formerly puzzling and at one time more or less shrouded in a prudent veil of mystery, and the reader who is interested in the detailed theory of this most fascinating branch of chemistry will do well to consult some of the recent monographs dealing more exclusively with this side of the subject, and also the Reports of the Faraday Society and of the American Committee on Contact Catalysis.

The present book, in its attempt to give a systematic survey of the industrial applications of catalysis, is likewise concerned with the fundamental theory upon which the technical science depends ; but it is only possible to offer in as condensed a form as possible a summary of the present state of knowledge and general opinion.

Academically there has always been a tendency to divide catalytic actions into the obvious categories of those which take place in a homogeneous system and those which are heterogeneous (that is to say, broadly, those in which a solid catalyst effects chemical change

in a liquid, liquid and gaseous, or gaseous system). It is usually the custom to discuss the apparently simpler case of homogeneous catalysis before proceeding to that in heterogeneous systems, but the trend of recent work has been so much in the direction of better understanding of heterogeneous contact actions that it seems quite possible that (at all events in the case of a condensed summary) a clearer conception of the subject will be arrived at by taking the heterogeneous class first.

The next chapter is therefore devoted to an outline of present-day views on contact action at solid surfaces and is followed by a chapter on the theoretical aspects of enzyme action, which is closely related to the previous case. A chapter on homogeneous catalysis follows, and it may be said here that, although this field was, until recently, probably more thoroughly explored than actions at solid surfaces, and the general conditions governing the rate of reaction, etc., were fairly well understood, the actual mechanism by which a catalyst operates in a homogeneous system is not yet so clear as in the other case, and the knowledge gained from the study of heterogeneous actions may well afford insight into the precise function of catalysts in homogeneous systems.

#### Classification of Industrial Catalytic Processes.

The formal orientation of catalytic actions into homogeneous and heterogeneous divisions is more or less essential for consideration of the theory of this branch of chemistry, and it also serves as the most suitable general basis for grouping the manifold industrial applications of contact action. The remaining Sections of this book are concerned with technical processes, which, broadly speaking, may be classified as catalyses at solid surfaces, fermentation methods, or catalyses in homogeneous systems; they thus correspond in some measure with the theoretical aspects which are referred to in Chapters II, III, and IV of this Section.



The order of treatment has been determined by several considerations. The heterogeneous actions, or catalyses induced by solid surfaces, are the most numerous class, and also include many of the most important instances of industrial catalysis, both from the standpoint of output and also from that of the intrinsic value of the products to the community; consequently they have been given pride of place.

The following Section (III.) is devoted to a short survey of technical processes which are governed by enzyme action. This procedure, which involves a break in the logical treatment of the purely chemical methods, is intended to focus attention on two points: (i.) these biochemical catalyses are intermediate in character between the heterogeneous and homogeneous systems of purely chemical catalysis, since they are surface actions which frequently take place in an apparently homogeneous medium; and (ii.), more important, they are processes which are not only catalytic (*i.e.*, avoid the use of extra chemical reagents), but also proceed at or near to the ordinary temperature, with consequent large economy in fuel costs. Emphasis has already been laid (p. 8) on the desirability of exploring biochemical methods of chemical change wherever possible, in order to arrive at manufacturing processes which combine elimination of auxiliary chemicals with economy in heat energy. It is, of course, unreasonable to expect that ordinary technical chemical methods will be superseded eventually by controlled enzyme action, but the growing list of chemical compounds manufactured by fermentation processes indicates that this branch of applied catalysis is worthy of continued and intensive investigation, and that in many specific instances its employment may be expected to receive considerable extension.

Section IV. deals with catalytic actions which proceed in a homogeneous (liquid) system, a category which includes many important technical processes, both old and new. It is not so diffuse in general

method, and does not contain so many instances of huge outputs of heavy chemicals, as the heterogeneous section ; but it embraces many technical methods of hydration, dehydration, and esterification (including the production of ether, glucose, acetic acid, esters, etc.), as well as various other kinds of chemical change.

It will be found, here and there throughout the book, that the formal division into heterogeneous and homogeneous catalyses has not been strictly observed. This happens in a few instances in which both forms of catalysis have been proposed in order to obtain the same product, or to effect the same process ; in such cases it is obviously convenient to consider both types at the same place in the volume. Generally speaking, however, the system adopted is as stated in the preceding paragraphs.

The treatment of technical catalytic actions according to their general character in this way has, it is felt, conferred a certain amount of order upon the general scheme of the book. At the same time, readers interested in the manufacture of a particular chemical may wish to be directed more immediately to the pages in which its catalytic production is discussed. The chief processes mentioned in this book have therefore been tabulated (pp. ix-xxii, following the Table of Contents), first, in the order in which they are treated, next, with primary reference to the product of manufacture in each case, and, finally, with reference to the different catalysts employed.



## CHAPTER II

### THEORETICAL ASPECTS OF CATALYSIS AT SOLID SURFACES

UNTIL about 1920-1925 there was a distinct conflict of opinion as to the mechanism by which a solid catalyst effected chemical change in gases or liquids; the rival views may be referred to briefly as the physical and the chemical (or intermediate-compound) theories of heterogeneous catalysis.

Physical explanations of catalysis were first based on the fact that porous materials (*e.g.*, platinum or charcoal), which accelerated such actions as the union of hydrogen and oxygen, possessed the capacity for concentrating gases in a layer at their surfaces, with accompanying thermal effects similar to those observed in the liquefaction of a gas. It was therefore concluded by van't Hoff<sup>1</sup> that the gases were brought into a state of compression and abnormal concentration by the catalyst, with the result that chemical action was enormously accelerated without any direct chemical intervention of the catalyst. At this period the gaseous concentration or adsorption was regarded as a "diffusion layer" several molecules thick, at the solid surface, the rate of chemical interaction being a supposed function of the rate of diffusion in this layer, and not depending on any actual chemical change at the surface of the catalyst.

As Sabatier<sup>2</sup> has emphasised by two clear-cut examples, this view fails to account for varying chemical action exerted on one and the same substance by different materials: isobutyl alcohol, which when passed over copper at 300° yields isobutyl aldehyde and hydrogen, by passage over alumina at the same temperature gives isobutylene and water, and over uranium oxide at the same temperature a mixture of

all four substances. More striking still, formic acid is decomposed by one oxide, that of zinc, into hydrogen and carbon dioxide, and by another (titania) exclusively into carbon monoxide and water. A more recent instance of exactly the same kind is the combination of carbon monoxide and hydrogen in presence of different materials; with nickel, methane is formed almost exclusively, with zinc oxide or chromate, quantitative yields of methyl alcohol can be obtained, whilst with an iron-alkali catalyst a mixture of higher alcohols, ketones, and hydrocarbons is formed.

Similarly, purely physical theories of this type fail to account for a phenomenon which is often met with, namely, the markedly selective action of many catalysts together with their power of producing isomeric or other change, which, as will be shown a little later (p. 19), is absolutely clear evidence that chemical inter-relationship of an intimate nature has occurred between catalyst and organic molecule.

On the other hand, the investigations of the late Lord Rayleigh,<sup>4</sup> Sir W. B. Hardy,<sup>5</sup> Irving Langmuir,<sup>6</sup> and others defined more clearly the physical nature of adsorption, and showed that, whilst a "diffusion layer" of adsorbed molecules may exist in many cases, the primary condition of adsorption of a gas at a solid surface is due to a single layer of molecules which (according to Langmuir) are held at the surface by a force which is indistinguishable in effect from chemical force or affinity. In this form the physical or adsorption theory of catalysis, which has been closely studied in recent years by a number of workers, including especially the members of the physico-chemical department of the University of Princeton, U.S.A., approaches very close to the corresponding development of the older "intermediate-compound" view of advocates of chemical theories of catalysis.

A chemical or "intermediate-compound" theory of catalysis was first put forward by de la Rive and Marcet<sup>7</sup> in 1828, and was considerably elaborated by

Berthelot<sup>8</sup> in 1880, in connection with the catalytic decomposition of hydrogen peroxide. Williamson's<sup>9</sup> investigations of the dehydration of alcohol by sulphuric acid and Squibb's<sup>10</sup> work on the conversion of acetic acid into acetone by passage over barium carbonate are examples of catalysis in which the intermediate compounds between catalyst and organic compound (ethyl hydrogen sulphate or barium acetate) are capable of isolation.

P. Sabatier and A. Mailhe<sup>11</sup> tabulated the action of a large number of metallic oxides upon ethyl alcohol vapour at 300°, and showed that certain oxides (*e.g.*, manganese or tin) are almost exclusively dehydrogenating in action, giving only acetaldehyde and hydrogen, while others (especially thoria and alumina) are entirely dehydrating and yield only ethylene and water. Others, *e.g.*, uranium oxide, cause both dehydration and dehydrogenation to take place. *The chemical action induced by a catalyst is specific to the chemical nature of the catalyst.*

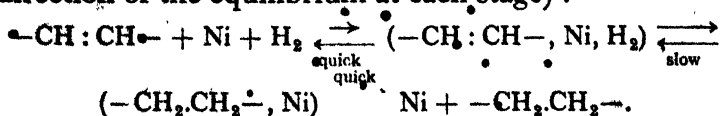
Sabatier attributed hydrogenation to the intermediate formation of unstable hydrides of the metallic catalyst employed, and was thus a supporter of the chemical or "intermediate compound" theory of heterogeneous catalysis; but here he abandoned the conception of complex formation between organic compound and metal, and only considered the possibility of union of hydrogen with the metal.

The advent of technical fat-hydrogenation about 1910 resulted in much further progress in the theoretical understanding of heterogeneous catalysis. It became clear in the first place that Sabatier's conception of union solely between nickel and hydrogen was too narrow, and that the organic compounds concerned in the process—the unsaturated fats—themselves were intimately connected chemically with the catalyst. The first and most obvious evidence of this was the observation that "iso-oleic" glycerides were produced during hydrogenation of fats. C. W. Moore<sup>12</sup>

showed in 1919 that, from oleic glycerides, the iso-oleic compounds produced were mainly elaidic (the geometrical isomeride of oleic) compounds, accompanied by small proportions of glycerides of acids in which the double bond had been displaced along the carbon chain; T. P. Hilditch and N. L. Vidyarthi<sup>13</sup> later showed that these structural isomers of oleic or elaidic acid were *cis*- and *trans*- forms of the  $\Delta^{8:9}$ - and  $\Delta^{10:11}$ -octadecenoic acids.

Furthermore, addition of hydrogen is frequently selective. In a polyethenoid compound one double bond is often reduced preferentially to another; in mixtures of monoethenoid compounds one of the latter is frequently attacked in preference to another. This phenomenon of *selective hydrogenation*, first observed by G. Vavon<sup>14</sup> and by C. Paal<sup>15</sup> in 1911-1912 in the terpene and aromatic series, is very important from the standpoint of the technologist. It is, at the same time, a further and cogent argument that the catalyst and the organic compound (as well as the hydrogen) are intimately and directly connected during the hydrogenation process.

In 1919, E. F. Armstrong and T. P. Hilditch<sup>16</sup> showed that catalytic hydrogenation in a liquid system is an action of the "uni-molecular" order, equal amounts of a pure unsaturated compound being hydrogenated in equal times at any stage of the process. This observation, which has been confirmed by E. B. Maxted<sup>17</sup> and by other investigators, can be interpreted only on the hypothesis that the unsaturated organic compound and hydrogen are both associated with the catalyst in the form of an unstable (not necessarily isolable) complex; the whole process was represented by the following scheme (in which the size of the arrows is meant to indicate the general direction of the equilibrium at each stage):—



The concentration of the reacting masses, whose rate of transformation is actually measured, is at all times very small in comparison with the total concentration of unsaturated compound or of hydrogen or of saturated compound present in the system as a whole.

At the same time, investigation of the adsorption of hydrogen, nitrogen, helium, carbon monoxide and dioxide, ethylene and other gases at the surface of catalytic nickel, copper and other metals was being carried out, notably by H. S. Taylor<sup>18</sup> and his co-workers at Princeton, U.S.A. It was found (i.) that metallic catalysts of this kind adsorbed much less nitrogen or helium than hydrogen, and (ii.) that ethylene and carbon monoxide were adsorbed to about the same extent as hydrogen. Subsequently, also, these investigators observed that the heat of adsorption of gases such as hydrogen or ethylene was of quite a different and increased order from that of gases such as nitrogen or helium which did not take part in catalytic chemical changes.

The recognition of two distinct kinds of adsorption, the purely physical or "condensation" effect accompanied by relatively small heat changes and the "activated adsorption" or "chemi-sorption" characterised by much greater heat changes is now well established as the result of the work of E. K. Rideal and many others in addition to those mentioned above. It has served to reconcile in large measure the two formerly opposed views of physical adsorption and of formation of intermediate compounds. Definite intermediate chemical compound formation is probably rare in heterogeneous catalysis, but these catalytic actions are invariably preceded, or initiated, by "activated adsorption" by the catalyst of the reacting compounds. This adsorption resembles, and may be accompanied by, ordinary physical adsorption at the surface, but differs from it in the greater heat of "activated adsorption." The heat evolved is of the



order of a mild chemical reaction, and the forces involved are indistinguishable from those which we term chemical affinity. Moreover, the layer of the molecules thus held by "activated adsorption" at a catalyst surface has in many cases been shown to be unimolecular.

In this form the "intermediate-compound theory" coincides in most respects with the physicists' "unimolecular layer" adsorption theory, and from this point the development of the general modern view of catalytic action can best be dealt with on the basis of the unified views: for the physicists have come to the conclusion that the adsorption processes concerned in catalysis are conditioned by forces indistinguishable from chemical affinity and are mainly concerned with unimolecular layers, whilst at the same time chemists have come to appreciate that an association of the organic molecules with the solid catalyst occurs which is at least equal in general character to, for example, the association between hydrogen and a catalyst.

The alteration of activity produced in a solid catalyst by exposure to high temperatures has been a fruitful source of observation with regard to adsorption and other properties of the catalyst. The workers at Princeton showed that a catalyst, prepared at a low temperature and capable of adsorbing a definite amount of interactant, adsorbs less of the latter after exposure to a somewhat higher temperature, and progressively less and less after heat treatments at successively high temperatures, thus suggesting that an action analogous to sintering takes place with resulting diminution in the number of active points in the catalyst surface. Armstrong and Hilditch<sup>19</sup> (*v. infra*, p. 29) have shown that, in unsupported nickel catalysts, exposure to high temperatures results in a given mass of reduced catalyst occupying a smaller bulk, and that there is a close parallelism between the "bulk gravity" of such catalysts and the activity which they display in actions of hydrogenation.

Taylor,<sup>20</sup> from consideration of all the foregoing observations on rate of hydrogenation, adsorption capacity of catalysts, thermal adsorption data, behaviour of catalysts to heat and "poisons," etc., put forward a picture of the atomic condition of the surface of an active catalyst, which may be summarised briefly as follows: The X-ray examination of metallic hydrogenating catalysts has shown that these catalysts, even when prepared at low temperatures, possess the definite lattice structure of the crystalline material. This does not exclude the occurrence, however, of local excrescences or irregular formation of atoms at the crystal surface, and Taylor suggested that the structure of the typical catalyst surface may be characterised by groups of atoms which, here and there, are thrust irregularly above the normal surface of the crystal formation.

The points at which isolated or semi-isolated atoms are supposed to be situated are, according to this view, the seat of catalytic activity. This picture affords an adequate explanation of such matters as:—

- (i.) The importance of irregular surface in general;
- (ii.) The sensitiveness of an unsupported metal catalyst to increases of temperature which would increase the inter-atomic vibration sufficiently to cause the isolated atoms to take up more stable positions in the plane surface (a "sintering" effect far removed from any incipient liquefaction of the metal).
- (iii.) The action of catalyst poisons and probably of some catalyst promoters;
- (iv.) The possibility of interaction with other molecules owing to the affinities of the exposed atoms being less saturated by neighbouring atoms, and consequently making these atoms more "unsaturated" or active and inclined to enter into chemical relation with other molecules.

There is some evidence, although it can hardly be regarded as conclusive, which indicates that at the moment of actual catalytic action the active atoms in

Taylor's theory may be actually detached from the surface, thus attaining to a state in which a definite "intermediate-complex" of an atom of catalyst and the interactants has a momentary existence. This view, if not essential to the theoretical explanation of the catalytic process, is further compatible with the approximation of such exposed atoms to the "gaseous" state in their thermal behaviour during adsorption, and with the observation of Hulett and Berger<sup>21</sup> on the minute but definite loss in weight of platinum when heated in oxygen.

This conception of the catalyst surface may also be considered in conjunction with selective action, and it may be hazarded that, for example, during selective hydrogenation that ethylenic centre which is preferentially saturated is probably *not* the one which is most strongly held at the nickel surface. The more strongly adsorbed of two unsaturated groups is probably less prone to saturation; chemical change would then tend to occur at the weaker attachment between the remaining double bond and (presumably) some other exposed nickel atom at the surface. The observation of Pelly,<sup>22</sup> that in a mixture of neutral fat and free fatty acid the free fatty acids are hydrogenated preferentially to the neutral fat, reinforces this view. It is generally agreed that the carboxyl group of an organic acid has a strong attraction for catalytic nickel, and it thus appears that those molecules which are, so to speak, anchored at the nickel surface by the free acidic radical are in a position to undergo saturation of the double bond more readily than are neutral esters.

In order to illustrate the general mechanism of catalytic action at a solid surface concisely and rapidly, the work of the Princeton school, and of a few other investigators who have studied more particularly the phenomena of hydrogenation, has been dwelt upon in some detail. It should, however, be stated that many other workers have contributed towards the present

knowledge of this branch of theory, including Constable, Hinshelwood, Rideal, Bancroft, Adams and co-workers, etc., etc.

We have thus a much clearer idea now than formerly of the general mechanism by which catalytic actions proceed at solid surfaces; but it cannot be said that an ultimate explanation has been found for these phenomena. Various theories based on the electronic structure of the atom, on the arrangement of the lattice of the solid atoms, or on other fundamental considerations, have been put forward by a number of authors since Taylor gave his "picture" of the catalyst surface; the validity of these in most cases remains to be determined.

Constable<sup>23</sup> studied the surface of metals and metal oxide films on metals by a spectrophotometric or "interference" method, and inferred the presence in catalyst surfaces of specially active areas or patches; he concluded that the experimental facts of adsorption and catalysis can be explained quantitatively on the assumption that strong specific fields of force emanate from special configurations of atoms on the catalyst surface. Constable's conclusions seem to be not very different from those of Taylor, except that he does not postulate the existence of atoms extruded or semi-detached from the main surface, but rather attributes the specific fields of force to special configurational arrangements of the atoms in the surface layer.

G. M. Schwab<sup>24</sup> and his co-workers took a view more definitely distinct from that of Taylor in suggesting that the centres of activity are not distributed over the whole surface, or located at "active points," except in so far as they lie on lines which are phase boundaries. Adsorbed molecules are considered to undergo "adlineation," i.e., crowding together at phase boundary lines in the surface. Microphotographical observations suggested that these phase boundaries were the crystal edges of the micro-crystals in the surface and in their later papers further evidence

was brought forward to support the view that the seat of catalyst activity resides in crystal edges, boundary lines in grain surfaces, or other surface derangements. This "topochemical" theory of contact action appears to be the most fruitful development of Taylor's original conception which has so far taken place.

O. Schmidt,<sup>25</sup> on the other hand, attributes catalytic hydrogenation entirely to the diffusion of hydrogen into the metal, followed by subsequent ionisation of the hydrogen. He considers that the action proceeds, not at active centres on the surface of the crystals, but within the crystals in the cracks or pores associated with the name of Smekal. According to Schmidt, it is not adsorbed, but absorbed gases which react. His views appear to stand in contradiction to much of the other work which has been published and, in attributing all hydrogenation effects to activation of the hydrogen alone, his theory cannot be said to take into account the effect of the catalyst on the molecules of reacting organic compounds. It resembles in this respect the older views of Sabatier which, as already pointed out, fail to explain the phenomena of selective hydrogenation or of concurrent isomeric changes induced by the catalyst in organic molecules which are capable of hydrogenation.

Frankenburger<sup>26</sup> has contributed a systematic study of heterogeneous catalytic processes with special reference to and critical treatment of the conception of energy of activation.

Balandin<sup>27</sup> advanced a "multiplet hypothesis" of heterogeneous catalysis, that is, that active centres in a catalyst surface will not in general attract every part of the reacting molecule with the same intensity, but will exert a preferential attraction on some part or parts of it. If all the centres attract by preference the same part of the molecule, there will be no tendency for the molecule to be broken up, and adsorption without reaction will occur. On the other hand, if there are present various types of centres, some

attracting one part of the molecule and some attracting another part, decomposition becomes possible. For actual change to take place, however, the different centres must not be too remote from each other, but should rather be arranged in groups ("multiplets") containing one or more centres of each type. It is supposed, for example, in the dehydrogenation of cyclohexane by platinum, that each multiplet consists of six platinum atoms; three atoms of the latter adsorb and bind two atoms each of carbon, whilst the other three each bind two atoms of hydrogen. This hypothesis thus presents an attempt to differentiate between specific parts of each "active patch" of a catalyst surface. It is interesting in that it tends to account for the highly specific nature of many heterogeneous catalyses in organic chemistry, but, at present, it is difficult to envisage experimental tests by which it might be suitably investigated.

Boeseken<sup>28</sup> put forward a "dislocation" theory of catalytic action, suggesting that catalysts act by activating the reacting compounds, and different catalysts may activate the same substance in different ways and produce specific "dislocations" or temporary polarities by a kind of induction. The main factor in chemical catalysis is, on this view, that of energy, and the catalyst would act in spite of, rather than because of, the production of intermediate compounds.

Whichever of these somewhat conflicting views may prove to be nearer the truth, we are at least on firm ground in insisting, as the result of the extensive studies of the past twenty years on the nature of a solid catalyst surface, that the catalyst must be regarded, not in the mass, but with respect to certain select atoms in the mass in which all the activity displayed is now believed to reside. In Taylor's words, "this picture supplies a reason for much of the mystery with which the subject of contact catalysis has been surrounded hitherto." For it shows that the properties of the contact agent are to be differentiated

from the bulk properties of the substance of which the catalyst is composed ; that it is rather the properties of the individual atoms or molecules of the catalyst, with the changes in these properties induced by position and arrangement in the catalyst particle, which are of importance in catalytic change." It follows, therefore, that the worker on heterogeneous catalysis is in the somewhat unique position of observing the behaviour of a selected few of the atoms or molecules present in the material under investigation, instead of dealing with the average behaviour of the whole assemblage of an enormous number of ultimate particles.

The recent work helps to emphasise the essential conditions of suitable surface which must obtain before any catalysis occurs : when a suitable surface is present, no catalytic action will occur unless on that surface (whether deposited or forming the total surface *per se*) there is a specific chemical adapted to adsorb or form appropriate intermediate compounds with the interactants ; for example, if hydrogen and ethylene are presented to such a surface no formation of ethane will occur unless there is present some specific material such as palladium, platinum, nickel or copper.

#### Essential Conditions of the Catalytic Surface in Practice.

The principles on which depend the practical formation and maintenance of an active catalyst surface become fairly obvious when approached from the standpoint of the preceding statement. Since catalysis is largely dependent on the surface at which the action takes place, it may be expected that colloidal sols would be the most active catalysts ; this, however, is not so, owing to the liability of the sol form to be affected by extraneous matter. Nevertheless, certain other colloidal materials (*e.g.*, gum arabic) have a stabilising or " protective " effect on the activity of a colloidal sol catalyst, although the protective colloid has also the effect of reducing the initial maximum activity of the sol.

In the case of solid surfaces somewhat similar phenomena are met with. Thus, confining ourselves again, by way of example, to the case of nickel, the finely divided metal *per se* is extremely sensitive to the influence of temperature; something akin to sintering takes place, the apparent volume of the metal is reduced and also the adsorption capacity for ethylene, hydrogen, etc. Evidently the exposed nickel atoms (employing Taylor's conception) are readily, so to speak, shaken down by relatively mild exposure to heat, so that a less irregular surface results with fewer centres of catalytic activity.

If, however, the nickel has been prepared by deposition as carbonate on an inert porous support (especially kieselguhr, or charcoal), an effect is obtained which is somewhat similar to that of a protective organic colloid on a catalyst sol, namely, the reduced supported nickel is able to withstand much higher temperatures than the unsupported catalyst without any serious alteration in activity; but, contrary to the case of the protective colloidal sols, the initial activity of the supported nickel is usually far greater than that of a corresponding mass of unsupported nickel. Exposed nickel atoms in a supported catalyst may well be separated from each other to some extent by intervening molecules of the irreducible support, so that the cohesive effect between the metal particles as a result of heat is much less pronounced.\*

These statements may be illustrated very briefly by the data in the following tables, which show: (i.) some relations between temperature treatment, apparent volume, and catalytic activity of various nickel preparations (Armstrong and Hilditch<sup>19</sup>), (ii.) the adsorption capacity for hydrogen of copper and nickel catalysts prepared at varying temperatures (Pease, Beebe and Taylor<sup>20</sup>), (iii.) the activity of a supported nickel catalyst with varying proportions of the nickel in a reduced condition (Armstrong and Hilditch<sup>19</sup>):



TABLE I

	Source of Reduced Nickel.			Reduced Nickel.			
	Sp. Gr.	Bulk Gr.	Temperature of Reduction.	Sp. Gr.	Bulk Gr.	Pyrophoric character.	Catalytic Activity.
Powdered fused nickel oxide.	6.96	0.35	500°	8.14	0.52	None	None
Precipitated nickel hydroxide.	5.41	0.87	300°	7.85	0.83	Pro-nounced	(a)
			500°	8.18	0.56	Medium	(b)
Corresponding oxide.	3.04	0.91	300°			Faint	(a)
			500°			None	(b)
Nickel oxide on diatomaceous earth.	1.63	3.22	500°	1.85	2.67	None	Very active

(a) Fairly active ; in vapour hydrogenation this type of nickel is capable of hydrogenating the benzene ring.

(b) Very little activity ; catalysts reduced at a lower temperature but above 300° are intermediate in activity between (a) and (b), and perform easy hydrogenations such as the saturation of a simple ethylenic linkage but fail to attack the aromatic nucleus.

TABLE II (Pease, Beebe and Taylor)

Catalyst.	Heat Treatment.	Adsorption of Hydrogen at 0° and 760 mm.
A. 100 gm. active Cu	No heat beyond reduction of oxide at 200°	3.70 c.c.
B. . . . .	"A" heated to 450° for 1.5 hours	1.15 "
C. 27 gm. active Ni	Obtained by reduction of oxide at 300°	35 "
D. . . . .	"C" heated at 400° for 4 hours	16 "

Dobuitchin and Frost<sup>30</sup> state, similarly, that the crystal nuclei of a palladium catalyst increased in size, as the catalyst "aged," from less than 40 to 250-1000 Å ; the total adsorption of hydrogen was unchanged, but the rate of adsorption and desorption was reduced. "Ageing" was produced by heating the catalyst in a vacuum at 0°-100° for 0-20 hours.

TABLE III

Nickel oxide deposited on diatomaceous earth, and containing a total concentration of 14.5 per cent. of nickel, was reduced in hydrogen at 450°–500° to varying extents. The relative activities of the products were measured roughly by the rate of absorption of hydrogen when linseed oil was hydrogenated at 180° with an amount of the catalyst such that the total nickel present was 0.1 per cent. of the oil; the following results were obtained :—

Per cent. Reduced Nickel.	Ratio of Reduced : Total Nickel.	Catalytic Activity.	
		H <sub>2</sub> Absorption Litres p. min.	Ratio. (Most Active Catalyst as Unity).
2.88	0.199	0.130	0.280
3.56	0.246	0.159	0.342
5.63	0.389	0.302	0.649
6.45	0.445	0.333	0.716
8.46	0.583	0.456	0.981
10.36	0.714	0.465	1.000
12.05	0.886	0.465	1.000
14.19	0.979	0.445	0.957

It is considered that figures of this nature indicate that the activity of a catalyst is dominated by the condition of the surface layer of reduced metal, since it is obviously this part of the catalyst mass which will be first reduced in hydrogen to the metallic state.

The use of supported catalysts is fairly widespread and will be referred to again from a more technical point of view at various points throughout Section II of this book. The above is intended to give a theoretical outline of the practical conditions governing active catalyst surfaces, and should be taken in conjunction with the subsequent part of the present chapter which deals with the theory of catalyst promoters (pp. 35–42).

#### Catalyst Poisons.

Some catalyst "poisons" (*e.g.*, hydrogen sulphide, or acids) may act by definitely and chemically changing

the catalytic metal, although the amount of a very toxic substance necessary to suppress the activity completely is far less than that required to combine in stoichiometrical proportion with the metal. Many other substances, however, exert a paralysing effect on the activity by covering up the catalytic surface and preventing contact between the metal and the other interactants. Thus Sabatier has pointed out that in a vapour hydrogenation process the merest film of condensed organic vapour on the catalyst is sufficient to stop all further hydrogenation.

Again, in liquid hydrogenation, especially in technical processes such as fat-hardening, where the materials to be treated are not pure chemical compounds, it frequently happens that impurities of a colloidal nature are present which are partially coagulated by the action of heat; such substances (resins, tars, mucilaginous matter, etc.), are naturally deposited on the solid catalytic material, and, whether chemically harmful or not to the metal, hinder the process by preventing proper contact.

In other cases, of which the "poisoning" action of carbon monoxide on nickel is a well-known example, the effect is not permanent and the activity is restored when the impurity has been displaced from the interacting system.

The picture of the mechanism of catalytic action afforded by the most recent theories on the subject (pp. 22-24) again helps considerably to an understanding of what goes on when a catalyst is "poisoned" or its activity is lessened by the presence of an added substance.

Catalyst "poisoning" is undoubtedly always due in the first place to the same factor, which precedes chemical change, namely, the formation of a unimolecular adsorption layer or unstable compound at the solid surface.

If the adsorbed material is a colloidal suspension or a liquid or solid such as resins, tars, etc., contact with

the other interacting substances will be prevented. If the adsorbed material has a pronounced chemical action on the surface owing to the production of a sulphide or other salt, the character of the surface is permanently altered and the catalyst destroyed; the reason that minute proportions of a strong "poison" such as hydrogen sulphide can suppress almost all activity is because the actual effective atoms of catalysts are relatively few in number and are in the most favourable position to form adsorption compounds of maximum permanence with approaching molecules of any kind, be they interactants or "poisons."

For example, it has been stated<sup>31</sup> that the smallest detectable trace (0.0001 per cent.) of hydrogen sulphide causes a 70 per cent. reduction in the activity in ammonia synthesis of an iron oxide-alumina-potash catalyst at 450°. The total number of molecules of hydrogen sulphide present will be insignificant when compared with the total number of atoms in even the surface layers of the catalyst mass, but is evidently comparable with the number of those atoms which are acting as effective catalysts.

The diminution of activity of palladium and platinum in presence of small proportions of certain adsorbed metals, which was carefully studied by Maxted,<sup>32</sup> can be readily understood from the same standpoint.

The same explanation holds for the poisons which do not, as a rule, proceed to form definite compounds with the component atoms of the surface. Pease and Stewart,<sup>33</sup> for example, have shown that a copper catalyst which is capable of adsorbing 1 c.c. of hydrogen has its hydrogenating activity reduced by over 90 per cent. if 0.03 c.c. of carbon monoxide is also adsorbed, although the adsorption capacity for hydrogen is not markedly altered. The carbon monoxide, which is adsorbed in preference to hydrogen, is evidently held mainly at those atoms which are most effective in hydrogenation.

With carbon monoxide, and no doubt in similar cases

where a definite stable compound is not produced, it is easy to understand that the poisoning action is rather of an "anæsthetic" than of a definitely "toxic" nature, for under suitable conditions the carbon monoxide can be displaced from the catalyst, the activity of which is then found to revert to the normal.

Although it is convenient to retain the old terminology of catalyst poisons and catalyst promoters (accelerators), it is really obvious nowadays that the main factor which determines both effects is that of selective adsorption of one or other component present in the interacting system. Formerly, of course, these effects appeared very complex, mysterious and difficult to understand, the amount of poison or accelerator necessary to produce very marked effects being so extremely small in comparison to the weight of reacting material, or even of catalyst. The operation of selective adsorption at a surface such as that outlined on p. 22 brings into line the phenomena of inhibition or poisoning, some of the means by which the activity of a catalyst can be apparently enhanced, and also cases of what is known as "beneficial poisoning"—all of these being different aspects of one and the same fundamental condition.

"Beneficial poisoning" is the case in which a catalyst reaction is slowed down by the presence of a specific material in such a way that the catalytic process stops short at an intermediate stage in the sequence of a possible chain of reactions. For example, Sabatier and others showed that when a mixture of acetylene and hydrogen in equal volumes is passed over catalytic nickel there is invariably obtained a mixture of ethane and unchanged acetylene, no ethylene being produced; work by Ross, Culbertson and Parsons,<sup>24</sup> however, has indicated that if the nickel surface is first saturated with acetylene alone and then treated with a mixture of acetylene and hydrogen, ethylene can be produced in some quantity. The covering of the entire nickel surface with adsorbed acetylene in the first instance

appears to restrict the adsorption of hydrogen with consequent retardation of the hydrogenating reaction.

Another excellent example of the utilisation of beneficial or protective poisoning is the preparation of aldehydes from acid chlorides by the method of Rosenmund, Zetsche and Heise.<sup>35</sup> These authors found that if benzoyl chloride in solution in pure benzene is hydrogenated in presence of colloidal palladium only traces of benzaldehyde are produced, whereas if ordinary benzene (containing thiophene) is used, good yields of benzaldehyde result. They extended their observations and found that substances such as quinoline, dimethylaniline or quinoline heated with sulphur all had similar good effects on the yield of aldehyde obtained in this reaction, whilst it was also found that the use of palladium on a support containing sulphur (*e.g.*, barium sulphate) assisted to the same end. The action here is to restrict hydrogenation to the comparatively simple replacement of chlorine by hydrogen, whereas in the absence of impurities in the system the resulting benzaldehyde would be further hydrogenated and/or polymerised. By employing palladium partially poisoned to varying extents, benzoyl chloride has been reduced to benzaldehyde, benzyl alcohol, benzyl benzoate, dibenzyl ether and toluene; most other acid chlorides behave similarly.

Finally, the employment of water as a protective poison may be noticed: this probably occurs in many processes, but has been particularly pointed out in the case of oxidation or dehydrogenation of alcohol vapours at the surface of metallic copper. Both the oxidation of methyl alcohol to formaldehyde, the decomposition of ethyl alcohol into acetaldehyde and hydrogen by copper, and the hydrogenation of acetaldehyde to alcohol in presence of nickel proceed with considerably improved yields of the desired products if a suitable proportion of water vapour is present in the system at the same time; it is presumed that the metal adsorbs the water vapour to some extent pre-

ferentially to the organic compound, with the result that side reactions of the latter are minimised.

In the course of describing many of the technical processes dealt with in Section II of this book, attention will be directed repeatedly to various phases of catalyst poisoning, all of which should be correlated by the reader with the general theory as illustrated in the foregoing paragraphs.

#### Catalyst Stimulants.

It has already been stated that the enhanced activity observable in some catalysts, in presence of minute amounts of added materials either in the reacting system or in the solid catalyst itself, is probably to be explained on the basis of selective adsorption. It should be noted, however, that in the cases in which this principle is utilised in technical practice it usually takes the form of the employment of what are known as mixed catalysts, that is to say, catalysts consisting of a major component with minor amounts of the accelerating or "promoting" substance. It may sometimes happen that a component of the system exterior to the catalyst has a definite accelerating rather than a retarding effect on the particular chemical change; thus it has been stated from time to time that the presence of small quantities of oxygen in hydrogen has a beneficial action on various hydrogenation processes, either by way of general acceleration, or by minimising the production of an undesired by-product. (For instance, the presence of about 0.2 per cent. of oxygen in the hydrogen used in the reduction of acetaldehyde in presence of nickel is said to prevent the formation of small quantities of ether in the resulting ethyl alcohol).

In the great majority of cases, however, acceleration or even apparent initiation of a definite catalytic change results from the presence of solids added to the main catalyst. The illustration of the mechanism by which these changes in behaviour are effected has not pro-

ceeded by any means so far as that of the action of poisons, but it appears most probable that the primary function of the added material ("promoter" or "stimulant") is to alter the general conditions of adsorption at the solid surface, with the result that the ensuing chemical change takes a different course. If we accept Schwab's theory that the main seat of activity resides in the phase boundaries (crystal edges, etc.) of a catalyst surface, it is clear that these boundaries will be altered in character, more or less profoundly, by the presence of incorporated solids. The virtues of a "promoted" catalyst may reside in the particular configuration of the phase boundaries which results from the admixture of specific materials with the main catalyst.

Evidently, therefore, this is a much more complicated case to investigate than that of the selective adsorption of different gaseous or liquid compounds at a relatively simple solid surface, and it is not surprising that it is somewhat difficult at present to distinguish the wood from the trees.

A few illustrations will be given in support of the above general statement, and in order to give some general indication of the possible mechanism of various mixed or promoted catalyst processes which will be referred to later in this book, from selected cases which have been studied from the theoretical point of view.

One general word of warning, however, may be offered to the student of catalyst promoters, namely, that the patent literature is crowded with claims for mixed catalysts of all kinds for the carrying out of all manner of processes. Certain of these patents, probably many of them, are undoubtedly the result of sound observation and form well-authenticated instances of catalyst stimulation; but there is no doubt that in many other cases the claims have not been sufficiently well studied, or have been multiplied considerably beyond what experimental facts may justify. Consequently the abundant information in



the patent literature cannot be accepted, in the case of catalyst promoters, as in any way suitable matter for the indiscriminate collection of data on which to base any explanation of the phenomenon.

(i.) *Mixed Metal Catalysts*.—These are amongst the first cases in which promoter action was definitely recognised. The Badische Anilin und Soda Fabrik,<sup>36</sup> in the early stages of their hydrogen and ammonia syntheses, investigated an enormous number of mixed metal catalysts for both processes and, for example, succeeded in replacing the more expensive uranium or osmium ammonia catalyst by iron, nickel or similar metal in association with a metal such as molybdenum or bismuth. •

So far as laboratory actions are concerned, Ipatiev<sup>37</sup> had published observations prior to the Badische work to the effect that the presence of iron favoured in some cases the activity of copper as a hydrogenating catalyst, and also that a mixed nickel-alumina catalyst could effect the combined hydrogenation and dehydration of, for example, camphor to camphene or phenol to cyclohexane at a temperature  $100^{\circ}$ – $150^{\circ}$  lower than that necessary for either hydrogenation over nickel alone or dehydration in presence of alumina alone.

Other cases of mixed metal catalysts (usually with one metal very largely preponderating) will be found in many other instances, but the information regarding them is largely empirical and does not indicate much as regards the mechanism of the promoter action.

One of the cases which has received detailed study is the reduction of copper oxide and of mixed copper-nickel oxides. Pease and Taylor<sup>38</sup> have examined the reduction of copper oxide at moderately low temperatures and have shown that the action proceeds practically entirely at a copper oxide-copper interface (reduction does not proceed freely until copper nuclei have been produced in the oxide mass). Armstrong and Hilditch,<sup>39</sup> examining the fact, recorded by Dewar and Liebmann,<sup>40</sup> that copper-nickel catalysts

could be reduced at or below about  $200^{\circ}$  with production of active catalytic nickel, showed that reduction of nickel oxide only occurred at the lower temperature (and active catalysts only resulted) when the copper and nickel had been precipitated together in the form of a double carbonate; thus the proximity of the copper and nickel oxides must be of a molecular order before reduction of the nickel takes place. These two sets of data taken in conjunction with each other offer some hints as to the interplay of one metal on the other in the catalyst surface.

(ii.) *Metal-Metal Oxide Catalysts*.—The cases in which a metallic catalyst has its properties altered or stimulated by the presence of traces of irreducible oxides are very numerous and may be divided into two classes, namely, those in which the oxides are of a neutral or feebly acidic type, and those in which they are definitely alkaline. We will consider the former class first of all.

- One of the most carefully studied cases so far is the influence of small quantities of oxides such as silica, alumina, thoria, iron oxide, etc., on the activity of hydrogenating catalysts, especially nickel. It has been established that the presence of very small percentages (1–2 per cent.) of alumina or silica co-precipitated with an unsupported nickel catalyst produces the dual effect of very materially increasing its activity and also of appreciably increasing its stability, especially with regard to the effect of temperature. The apparent volume of such promoted catalysts appears to be in general greater than that of pure nickel, and the adsorption capacity of such catalysts for ethylene, hydrogen, etc., is similarly increased. Beyond this it cannot be said that there is any clear experimental evidence concerning the mechanism of the stimulation in activity.

Reference should again be made here to the case of supported catalysts; for example, nickel mounted upon powdered pumice, fuller's earth, diatomaceous earth,

powdered silica gel or charcoal, etc. With the exception of the last, all these supports consist essentially of oxides of the type that we are considering at the moment, but their influence on the catalytic activity of the nickel differs widely. For example, nickel mounted on charcoal, pumice and most types of fuller's earth is little less sensitive to temperature than unsupported nickel, and its activity is not materially enhanced (except in the case of activated charcoals of the modern type). Here it appears that there is little or no mutual influence between the ultimate particles of the support and of the nickel, the former serving merely as a mechanical basis for the nickel and aiding in mechanical properties such as ease of passage of gas, ease of filtration, and so on. On the other hand, the highly activated charcoals, most kieselguhrs or diatomaceous earths, and also powdered silica gels have a very marked stabilising action on the resistance of the catalyst to higher temperatures, and also an equally marked effect on the temperature of reduction of nickel oxide deposited on these materials.

For example, a temperature of  $350^{\circ}$ – $400^{\circ}$  may be required in order to obtain efficient reduction of nickel on an active charcoal, whilst on kieselguhr at low concentrations (10–20 per cent. Ni) reduction does not set in vigorously below  $420^{\circ}$ – $450^{\circ}$ , and in similar cases with silica gel as a support a temperature of  $550^{\circ}$  or even higher may be necessary for reduction.

Again, the composition of the oxides forming a porous support of the type of kieselguhr has considerable influence on the activity of the resulting catalyst; nickel mounted on a pure silica diatom structure is usually distinctly less active than if alumina is present in or has been added to the diatomaceous material. It therefore appears that the influence of the added oxide is largely specific, although it is not known yet with any precision what occurs in the actual promoted catalyst surface. Taylor's view on the basis of his picture of the catalyst surface would appear to be that

the presence of oxide molecules, adjacent to or interspersed among the nickel atoms in the outer layers of the catalyst, not only serves to diminish cohesive attraction between the metal atoms but also exerts specific selective adsorption effects, due to the adsorption capacity of the oxide "ions" in conjunction with that of the nickel atoms.

(iii.) *Metal-Alkali Catalysts*.—These form another important group of promoted catalysts, since the most common type of catalyst at present employed in ammonia synthesis consists of reduced iron coupled with an alkali such as sodium carbonate, potassium carbonate, lime, etc., in small quantities. The action of the alkaline oxide is not simple to explain, but the adsorption and other physical phenomena of an alkali-promoted iron catalyst exhibit corresponding parallelisms with the increase in efficiency over the pure metal catalyst.

Kunsmann<sup>41</sup> has compared the thermionic emission and the heats of activation of pure iron and iron-alumina-alkali catalysts, and finds that the emission of positive ions and the heat of activation are greater in the case of the more active composite catalyst; he concludes that the primary effect of the promoter is to increase the number of atoms at which catalytic action takes place.

Another case which is more readily understandable on chemical grounds is the influence of an iron-alkali catalyst on the union of carbon monoxide and hydrogen, when the formation of condensed chain compounds containing up to eight or nine atoms of carbon is observed; the tendency to condensation can readily be understood as a result of the intervention of alkali in the chemical changes involved, on lines discussed in dealing with the "synthol" process in Section II, Chapter III (pp. 110-113).

Finally, notice may be taken of the advantageous effect of the presence of a very small amount of sodium carbonate in the hydrogenation of liquid phenols by

nickel. The maximum effect is apparently reached when the alkali concentration is about 25 per cent. of that of the free metallic nickel present, and the rate of hydrogenation becomes more nearly linear than when the alkali is absent. This implies that in some way the nickel is being kept more free from toxic action, and it may be that the acidic action of phenol on the nickel is in some way restrained by the presence of adsorbed alkali.

(iv.) *Mixed Oxide Catalysts*.—Considerable attention has been paid to the theoretical study of mixed oxide catalysts in the case of mixtures of oxides of iron, chromium and cerium, or of manganese and copper, or of manganese, copper and silver; these mixtures very readily convert carbon monoxide to dioxide in presence of atmospheric oxygen.

Another important case of mixed oxide catalysis is the production of methyl alcohol from water-gas in presence of zinc oxide. Zinc oxide alone was at first discovered to be a reasonably active catalyst for this change, but later it was found that combinations of zinc and chromium oxides were far more efficient than the former alone, and more efficient than various mixtures of zinc with other oxides; recent work by Taylor and Kistiakowsky<sup>42</sup> has again demonstrated that the most efficient catalyst (zinc chromate) has by far the greatest adsorptive power of the series with respect to carbon monoxide, hydrogen and methyl alcohol.

Another important case of the use of mixed catalysts is that of "copper chromite" (prepared by reduction of basic copper chromate) in the conversion by hydrogen at 250 atmospheres pressure and about 300° of higher aliphatic acids or esters to the corresponding alcohols (Section II, Chapter XI). If reduced basic nickel chromate is employed, further reduction to hydrocarbons takes place to a considerable extent (Böhme<sup>43</sup>; Schrauth *et al.*<sup>44</sup>; Adkins *et al.*<sup>45</sup>).

The connection between adsorptive capacity and

the action of catalyst promoters is indeed sufficiently clear, although precise understanding of the details of the stimulatory processes involved is not yet forthcoming.

Other important cases of mixed metallic oxide catalysts are those used in certain oxidation processes, notably the German processes for the oxidation of ammonia to nitric acid, in which a mixture of iron oxide with a little oxide of a metal of variable valency (usually bismuth) forms the catalyst. The mechanism of promoter action in this case will no doubt eventually be brought into line with that of hydrogenating and other catalysts; all that may usefully be said at the moment is that it is evident, both in this and other cases of oxidation, that the presence of an element which has the capacity of more or less readily forming a series of oxides (*e.g.*, manganese, cerium, vanadium, bismuth, etc.) is invariably connected with the stimulation of catalytic oxidation.







## CHAPTER III

### THE ACTION OF ENZYMES

THE study of chemical actions effected by living organisms has naturally been prosecuted most largely in connection with physiology and pathology, and has consequently developed on somewhat different lines from those on which, for example, catalysis at solid inorganic surfaces has been investigated. Nevertheless it is now agreed that chemical actions conditioned by living organisms are effected by biochemical catalysts to which the generic term enzyme has been given, and that the general principles on which the latter act are substantially the same as those which govern any other form of catalysis. Investigation of the behaviour of enzymes is, however, more complicated and difficult than that of a solid inorganic catalyst, because the enzymes are only produced by living cells, they are far more complex in composition and specific in their action than inorganic catalysts, they exist in the form of colloidal solutions and are very delicate and exceedingly sensitive to the influence of temperature or extraneous chemicals. Thus their activity is, in general, retarded even by accumulation of the products of the chemical action which they induce or accelerate.

We have merely to consider the cases in which enzyme action is, or may be, employed as a means of manufacturing chemical compounds in bulk, and to this end it is sufficient to dwell on those aspects which determine the general conditions under which successful technical operation of enzyme actions is most likely to be realised. The vast literature on the function of fermentation processes of all kinds in the animal or plant organism does not concern us except in so far as it assists in the exploitation of specific ferments or

enzymes in the factory ; those who are interested in more general aspects of enzyme action will turn to treatises such as " The Nature of Enzyme Action " (Bayliss), or other appropriate monographs.

The nomenclature used by biochemists differs to some extent from that familiar to the ordinary technician, and a few definitions may be inserted at this point.

The term *ferment* was formerly applied generally to living organisms (such as yeast, fungi, bacteria or specific parts of more complex living bodies) which possessed the power of effecting chemical change in a compound (such as starch, sugar or protein) ; when it became recognised that the active chemical agent was not the living cell or organism itself, but a component of the latter, usually soluble in water, and certainly separable from the living matter, the active agent was referred to as a soluble or " unorganised " ferment, or, in modern phraseology (Kühne<sup>1</sup>), as an *enzyme*. An *enzyme* is therefore a biochemical catalyst (Effront<sup>2</sup>), and consists of a very complex colloidal organic molecule, which is not living (protoplasmic), but which is only producible at present by a living organism.

Enzymes are classified largely according to the type of compound upon which they exert chemical action. Broadly speaking, we are dealing with a catalytic system in which the catalyst is an *enzyme* : the substance acted upon is often referred to as the *substrate*, although other terms are used. For example, in actions of hydrolysis (e.g., cane sugar to invert sugar), the compound hydrolysed is called the *hydrolyte*. The general action of an enzyme is often referred to by adding the suffix *-lytic* to the generic name of the substrate ; etymologically it is preferable to use the suffix *-clastic* (H. E. Armstrong<sup>3</sup>). Thus a starch-fermenting enzyme is *amylolclastic*, one which decomposes protein is a *proteolclastic* enzyme, etc.

The individual names of enzymes are partly fortuitous, partly rational. The older, better-known bodies

received specific names, such as diastase, pepsin, trypsin, emulsin, etc., which have become more or less fixed by long association; incidentally, some of these probably consist of mixtures of enzymes. Latterly it has become usual to follow the suggestion of Duclaux, namely, to denote a specific enzyme by adding the termination *-ase* to that of the particular substrate acted upon; thus lactase is the enzyme which hydrolyses lactose, urease that which decomposes urea, and so on.

It has already been said that enzymes are colloidal in nature: in consequence a solution of an enzyme in water consists of a dispersion of the colloidal particles throughout the liquid phase, and behaves as a heterogeneous, rather than a homogeneous, system. It will be shown below that the study of enzyme action has proved to be that of an operation which is taking place at a surface, namely, the interface between the colloidal enzyme and the substrate solution. Thus, from the point of view of catalysis, the process falls into line with the heterogeneous actions discussed in the preceding chapter.

The colloidal, complex nature of the enzymes has made it, however, hitherto impossible to isolate any one of them in a pure condition. Other colloidal compounds are invariably present along with enzymes in the cell, and the product usually obtained is a preparation of which the active enzyme forms only a (frequently subsidiary) proportion. "Crystalloid" compounds which are also present in the cell-juices can be removed to a large extent by dialysis, and advantage can sometimes be taken of the differing electrical charges of the colloidal components of the mixture to effect some separation by selective adsorption on an electro-positive (*e.g.*, aluminium hydroxide), or an electro-negative (*e.g.*, kaolin) inorganic material. By combination of such methods Willstätter and co-workers have prepared relatively concentrated specimens of amylase, invertase, lipase, peroxidase and

trypsin, the activity of which was found to be many hundreds of times that of the starting-out material. Even in the most highly active products, however, it has hitherto proved impossible to assign any definite chemical composition to an enzyme, and it is doubtful if a close approach to the isolation of a pure enzyme has yet been effected. Consequently it would appear that the activity of an enzyme *per se* is extraordinarily high, and may, if it is possible to make the comparison, be intrinsically greater than that of an inorganic catalyst surface.

However this may be, it is certain that the specificity of action of enzymes far surpasses that of the ordinary inorganic catalyst; in general, the action of an enzyme is restricted to a few closely-allied kinds of—or even to one single—substrate. Of many possible instances, the familiar one of the hydrolysis of the stereo-isomeric  $\alpha$ - and  $\beta$ -glucosides is probably still as striking as any; the only difference between these lies in the configuration of the hydroxyl group which is concerned in the formation of the glucoside, yet whilst  $\alpha$ -glucosides are hydrolysed by maltase but not by emulsin, the reverse holds for  $\beta$ -glucosides, which are readily attacked by emulsin but not by maltase.

It is a frequent occurrence in metabolic changes that a specific transformation of a given compound is effected by a definite enzyme, which is produced at the seat of action and may only be effective for the particular change in question. In other cases, especially where the chemical change concerned is a relatively simple one, such as hydrolysis, the same enzyme may be capable of acting upon a number of compounds, so long as the configuration of the molecule is compatible with the enzyme. Thus emulsin will hydrolyse the synthetic  $\beta$ -methylglucoside, nearly all of the many natural  $\beta$ -glucosides (such as amygdalin, salicin, quercetin, etc., etc.), tetramethyl  $\beta$ -methylglucoside and even  $\beta$ -methyl-*d*-isorhamnoside (derived from the methyl-pentose *d*-isorhamnose, containing a chain

of six carbon atoms and the same configuration as *d*-glucose); but it is without action on  $\beta$ -galactosides (differing from *d*-glucose in configuration) or on  $\beta$ -methyl-*d*-xyloside (*d*-xylose has a similar configuration to *d*-glucose, but is a pentose with a 5-carbon-atom chain). In a few instances an enzyme is more generally active; lipase, the enzyme present in castor oil and other seeds, for example, exerts hydrolysing powers on a comparatively wide variety of compounds belonging to the class of fats and other esters of the fatty acids.

It should be added that enzyme action is held to be generally reversible; for example, an enzyme which hydrolyses a compound is able, under suitable conditions, to build it up. This was shown for the maltose-glucose change by Croft Hill,<sup>5</sup> for the action of lipase by H. E. Armstrong and Gosney<sup>6</sup> and for glucoside hydrolysis and synthesis by the researches of Bourquelot and Bridel;<sup>7</sup> and has also been established in a number of other instances.

It should be noted that in most instances the products spoken of as individuals, *e.g.*, maltase or emulsin, are probably mixtures of two or more enzymes, each of which may have specific properties.

E. F. Armstrong compares the relation of enzyme to substrate with that of a glove fitted on a right hand: if the position of any finger be altered it is impossible to fit the glove; further, the glove will not fit on the left hand. Emil Fischer originally compared the relationship to that existing between a key and the lock for which it is made.

It is widely held at the present time that the ultimate enzyme molecule may be a complex, perhaps labile, colloidal system of high molecular weight, a (perhaps relatively small) part of which may consist of groups of atoms or radicals, whose configuration enables them to fit that of a specific substrate and whose chemical constitution is probably frequently related to that of the latter. On this hypothesis the reactive part of the

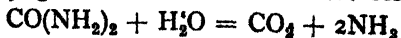
enzyme molecule might well be compared with a heterogeneous catalyst combined with a more or less inert support (*cf.* pp. 28, 39).

This leads us to the more general question of the kinetics and mechanism of enzyme action, the study of which has led biochemists to very similar conclusions to those reached by the workers in the field of contact actions at solid surfaces.

Measurement of the rate of chemical change effected by enzymes, in the hands of many workers, has given results of a complicated character. In many cases a considerable part of the change has appeared to follow a unimolecular or logarithmic course with respect to the disappearance of the substrate, but not infrequently the rate of action was observed to fall below that required for a unimolecular change as the fermentation progressed. Contrariwise, instances have been observed (*e.g.*, the work of Victor Henri<sup>8</sup> with invertase and cane-sugar) in which the rate was consistently greater than that of a unimolecular action. Such observations are now known to have been due to the operation of various conflicting factors, the nature of which will be explained a little later.

E. F. Armstrong,<sup>9</sup> in the case of hydrolysis of cane-sugar by enzymes (and also by acids), definitely showed, in a series of communications in 1904, that the shape of the hydrolysis-time curve was ideally linear, and that this was to be expected on the hypothesis of a combination between enzyme and substrate, whilst the relationship between the rate of reaction curve and the proportions of enzyme and substrate were likewise explicable on this basis. Similarly, in 1906, Bayliss<sup>10</sup> suggested that the rate of change in enzyme action is a function of the degree of adsorption of the substrate by the enzyme at different stages of the reaction.

The work of H. E. and E. F. Armstrong, Horton and others<sup>11</sup> in 1913 on the action of urease on urea



confirmed the fact that, if the products of the action were removed from the system and no conditions obtained which affected the activity of the enzyme preparation, the amount of decomposition per unit of time approximated to a constant figure throughout the whole of the reaction.

In other words, just as in the hydrogenating action of nickel studied at a later date (*cf.* p. 19), the essential rate of enzymic change is "nul-molecular," a constant amount of substrate being acted upon throughout in equal intervals of time. This has led H. E. Armstrong to express the opinion that "enzymic action takes place entirely at the surfaces of colloid particles suspended in the solution of the hydrolyte and not between substances which are all in true solution."

In the last (1925) edition of his "Nature of Enzyme Action," Bayliss sums up the mode of enzyme action as the sequence of (a) *diffusion* of the enzyme through the substrate solution (a relatively minor part), (b) *adsorption* of the interacting substances on the surface of the enzyme particles (practically instantaneous), and finally (c) actual chemical interaction between the substances brought together on the surface (usually the slowest of the processes concerned, and therefore that controlling the rate of action as a whole). It is unnecessary to stress the close correspondence between these views and those which have been arrived at on independent grounds in the case of the contact actions dealt with in the preceding chapter.

The tendency to combination with the enzyme (adsorption) is also shown to a marked degree by most of the products of enzyme action, and in appropriate circumstances the enzyme may be more or less put out of action owing to its adsorption of the products. Hence, as the latter accumulate, the effective concentration of the active enzyme falls off, leading to rate of action curves which frequently approximate to the logarithmic type. This was especially well illustrated

in the course of the studies of urease previously mentioned.

Again, increase in the concentration of the substrate beyond a certain point tends towards saturation of the enzyme surface by the latter, with consequent retardation of chemical change; consequently it is usual to find that enzyme action proceeds most readily when the substrate is in a state of considerable dilution—a point of some technical importance.

Other factors which influence the activity of enzymes include the acidity or hydrogen ion concentration of the solution and the amount of electrolytes present. Most enzymes are very sensitive to slight changes in the acidity or alkalinity of the solution, and are most active only at a definite point; the exact "hydrogen ion concentration" which is most effective varies according to the enzyme, the usual range being from media slightly more acid to media slightly more alkaline than pure water. (The hydrogen ion concentration of conductivity water is  $\frac{1}{10^{7.07}}$ , or  $10^{-7.07}$ ; employing the conventional expression introduced by Sørensen,<sup>12</sup> we say that water has the  $p_H$  value of 7.07, more acidic solutions having lower, and more alkaline solutions higher, values of  $p_H$ .)

The presence of electrolytes in solution usually has an appreciable effect on the general rate of action. This is doubtless related to the colloidal nature of enzymes, in consequence of which the effective surface of the particles may be expanded or contracted according to the concentration of electrolyte in the system.

The above factors are not definitely operative in the case of most solid or non-organised catalysts (of the types dealt with in the preceding chapter), but we come, in conclusion, to other causes of alteration in enzyme activity which are closely parallel with those affecting the ordinary contact agent in heterogeneous systems, namely, temperature, stimulants and toxic



agents (or, as the latter are termed in biochemistry, co-enzymes and anti-enzymes).

Enzymes are active only over a comparatively narrow range of temperature and exhibit maximum sustained activity at an optimum temperature characteristic for each enzyme. Enzyme action is practically negligible at  $0^{\circ}$ , but with rise of temperature the activity is increased from twofold to sevenfold for each increment of  $10^{\circ}$ . For most enzymes the optimum region of temperature lies at a point between about  $25^{\circ}$  and  $38^{\circ}$ ; certain bacteria which decompose some forms of cellulose are most active at  $68^{\circ}$ – $70^{\circ}$ , but this is quite exceptional. The *initial* activity of an enzyme continues to increase beyond the optimum temperature, but its *sustained* activity declines rapidly and, at a certain point (usually between  $70^{\circ}$  and  $100^{\circ}$ ), all activity ceases. Enzymes are destroyed by exposure to a temperature of the order mentioned, and it is believed that this is the result of a "coagulation" effect whereby the colloidal surface is destroyed. These phenomena were formerly held to differentiate enzymes from inorganic catalysts, although Ernst<sup>13</sup> showed that colloidal platinum sols exhibited exactly the same series of phenomena; as a matter of fact, however, very similar relationships between activity and temperature are observable in the case of solid contact agents (*cf.* p. 29), the only differences being the generally wider range of temperature over which activity is exhibited and the fact that these temperatures are of the order of, say,  $200^{\circ}$ – $500^{\circ}$  instead of  $0^{\circ}$ – $100^{\circ}$ .

The question of inorganic catalyst stimulants or "promoters" has been discussed in Chapter II (pp. 35–42). Parallel with this we have the influence of "co-enzymes" on enzyme action. In several instances it has been found that a substance (frequently crystallised and removable by dialysis) is always produced along with the enzyme, and that in its absence no activity is exhibited. Thus Harden and Young<sup>14</sup> found that the enzymes of yeast-juice, after separation

from the aqueous medium by expression on a gelatin filter, had no power to ferment sugar solutions, nor, of course, had the aqueous filtrate; but the fermentation proceeded normally when filtrate and colloid residue were again mixed. Similarly, liver lipase or pancreatic juice lose their specific activities after dialysis, but activity is resumed on adding to the colloid the dialysed liquid, or even, in some cases, solutions of specific salts. The mechanism of action of co-enzymes is little understood at present. Whilst the presence of a suitable electrolyte in appropriate concentration (*e.g.*, sodium chloride, potassium nitrate, or sodium phosphate) seems the main factor in some cases, in others this is not sufficient; thus filtered yeast-juice (zymase) is not restored to activity by the simple presence of a phosphate solution, although phosphates are necessary. There is reason to believe that the actual "co-enzyme" in this case is a hexose-phosphoric-acid ester.

Finally, enzyme action is retarded by many substances which are of the nature of "catalyst poisons" or "anti-enzymes." On the one hand there is some evidence that enzymes in a living body tend to the production of "anti-gens," *i.e.*, bodies which oppose their action; on the other there are abundant examples of the retarding effect of different chemical compounds on enzyme activity. Thus many proteins will retard the specific action of enzymes, such as emulsin or lipase, whilst these are equally or more susceptible to many simpler compounds such as, for example, hydrocyanic acid. It may well be surmised that these effects are conditioned by one or other of the following causes; selective adsorption or excessive general adsorption of the anti-enzyme at the active surface, changes in the colloidal state and surface of the enzyme induced by the presence of the anti-compound in the substrate solution.

Turning to the bearing of these observations on the practical applications of fermentation, it will be realised that the problems encountered will in many ways be

similar to those concerning inorganic catalysts, but the active agents are still more delicate and work within a more restricted range of temperature; beyond this, however, are the specific problems connected with the production and maintenance of an agent produced only from a living organism. In practice, up to the present, the use of enzymes apart from their living progenitors is the exception rather than the rule, and it is the more general practice to employ cultures of specific organisms or microflora which develop enzymes of appropriate properties. The most familiar example is the yeast plant, *Saccharomyces* sp., whilst the use of fungi, such as *Mycoderma*, or of bacteria, such as *Bacillus butyricus*, may be cited as typical instances of other classes of organisms. The technical production of enzymes is thus a problem of microbiology; it involves the selection of a medium in which the enzyme-content is maintained or replenished by adequate growth of the organism, and the exercise of precautions against infection of the medium by unwanted organisms different from the desired species.

Usually, therefore, in addition to the substrate it is necessary to provide specific nitrogenous material, inorganic salts, etc., in order to facilitate the growth of the enzyme-producing organism, whilst, as well as providing the necessary nutrients in this way, it is essential to carry out the fermentation process under rigorously sterile conditions. Furthermore, the various factors discussed above with reference to the presence of accelerating and retarding materials must be borne in mind.

Finally, the economic advantage of an enzyme process is, as has already been emphasised, largely bound up with the relatively low operating temperature, a temperature which, however, must be fairly closely controlled; whilst a possible disadvantage, in many cases, resides in the dilute solution of substrate, which is often necessary for vigorous fermentation, a factor which not infrequently leads to a still more dilute

solution of the ultimate technical products. In spite of these seeming difficulties there is undoubtedly scope for far more extended scientific application of these natural catalysts than has hitherto been made.

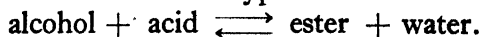
## CHAPTER IV

### THEORETICAL ASPECTS OF CATALYSIS IN HOMOGENEOUS SYSTEMS

QUANTITATIVE investigations connected with the theory of catalysis in homogeneous systems may be said to commence with Wilhelmy's famous study<sup>1</sup> of the rate of inversion (hydrolysis to glucose and fructose) of cane-sugar solutions in presence of mineral acids. He showed that the amount of sugar inverted at any moment was proportional to the quantity of sugar present at that time, and also that the rate varied according to the concentration of the acid and the temperature of the system. In the hands of Ostwald, Arrhenius and others the mathematical treatment of reaction velocity as conditioned primarily by the law of mass action was systematically developed, but the first example of a unimolecular action to be definitely analysed is to be found in Wilhelmy's work. In 1862 Löwenthal and Lennsen<sup>2</sup> made an important extension to this investigation by showing that the rate at which acids invert cane-sugar is proportional to the strength of the acids, and Arrhenius,<sup>3</sup> in connection with his electrolytic dissociation theory, showed that in sufficiently dilute solutions the rates of hydrolysis of cane-sugar or of simple esters conditioned by various mineral acids were exactly proportional to their degree of electrolytic dissociation into ions.

It thus became clear that the catalytic action of acids in hydrolysis was closely connected with the number of hydrogen ions present, the stronger, more completely ionised acids possessing high catalytic activity. Similarly, the work of Reicher<sup>4</sup> and others showed that the rate of hydrolysis conditioned by dilute alkali solutions was explicable as an action catalysed by hydroxyl ions.

The converse process of esterification was first studied from a similar point of view by Berthelot and St. Gilles<sup>5</sup> for a number of cases of simple, non-catalysed reactions of the type



The use of sulphuric acid as an esterifying agent had been practised for a long time prior to the realisation that its action was catalytic, and that, as shown by Victor Meyer and Sudborough,<sup>6</sup> and by E. Fischer and Speier,<sup>7</sup> it could be replaced with advantage in many organic preparations by the stronger and more active dry hydrochloric acid, employed in small proportions (*e.g.*, from 1-3 per cent. of the mixture of alcohol and acid). Senderens<sup>8</sup> and his colleagues demonstrated much later that not only sulphuric acid, but also anhydrous aluminium sulphate or potassium hydrogen sulphate, are also efficient esterification catalysts when present in quite small concentrations.

The above classical researches have led to an immense volume of experimental work by many well-known investigators on various problems related to catalytic esterification, dehydration, and hydrolysis in homogeneous systems, such as the constitutive influences exerted by one or both of the interacting organic molecules, the anomalous behaviour of strong acids and bases in other than small concentrations, and many similar factors. Other types of homogeneous catalytic action have received less frequent study from the kinetic standpoint, but reference may be made to Steele's examination<sup>9</sup> of the Friedel and Crafts condensation from this point of view; Steele was led to the conclusion that the action depended on the formation of unstable intermediate-complexes of the catalyst (aluminium or ferric chloride) with each interactant (aromatic hydrocarbon and organic halogen compound) and also with the organic product of the action.

In the case of processes involving the addition or elimination of water, it has been increasingly apparent that the simple ascription of catalytic power to hydrogen

or hydroxyl ions is insufficient to explain the observed facts, since it can only be quantitatively correlated with the latter in particular cases (namely, actions proceeding at great dilution with respect to the acid or base present).

Concurrently with the development of the Arrhenius theory, a considerable amount of work was carried out by H. E. Armstrong<sup>10</sup> and his students on processes operative in solution, their fundamental hypothesis being that hydrolytic action results from an interaction between the hydrated compound, which is being decomposed, with the hydrated catalyst. Armstrong regarded all chemical action as "reversed electrolysis," maintaining that a three-component circuit comprising the two interactants with a catalyst is in all cases essential to chemical action.

Simple kinetic studies of the rate of homogeneous catalytic actions, whilst useful in clearing the ground and indicating the general conditions operating, are not by any means entirely adequate to solving the problem of how the catalyst comes into play. The latter question is, indeed, more elusive in the case of homogeneous than of heterogeneous actions, because in the latter case it is possible not infrequently to choose conditions of observation which permit evidence to be gained as to what is going on at the catalyst surface itself, as distinct from the average behaviour of the whole of a homogeneous medium. Consequently the study of the function of a catalyst in a homogeneous system is much more difficult than in the other case, and it cannot be said that the explanations available up to the present are as explicit and generalised as in the case of contact actions (incomplete as the latter admittedly are). Investigation of the subject, moreover, is conducted on lines which, for the most part, are somewhat remote from industrial applications.

Attention is being increasingly directed to the question of how the interacting molecules in a homogeneous system are "activated" by the intervention of

a catalyst, *i.e.*, the manner in which energy is conveyed to the interactants. This fundamental aspect of catalysis goes, perhaps, more deeply into the matter than is necessary for the normal efficient application of catalysis in industry. Obviously, it is a most important—from a purely academic standpoint it is *the* most important—side of fundamental research into catalytic action, for it will ultimately tell us *why* catalysts display their specific activity. On the other hand, it would be ample aid for the moment if the technologist had at hand the fundamental data as to *how* catalytic action is effected in all cases; and it may be recalled that the late Sir William Ramsay used to impress upon his students that, when *why* was too difficult a problem to solve, *how* was frequently more tractable and quite helpful.

Only a very short sketch of recent academic investigations into homogeneous catalysis will therefore be added here.

Reverting again to the catalytic effects exerted by acids during esterification and hydrolysis, we find that Senter<sup>11</sup> observed that the effect of neutral salts on the activity of the acid catalyst, and also the general temperature coefficient relationships of the process, were not directly in accord with a simple hydration of the acid or the hydrolyte; on the other hand, his work and that of Lapworth<sup>12</sup> and others pointed to a specific action of water in the catalysis, and further, to the probability that the undissociated molecule of the catalytic acid also exerts a definite catalytic action in addition to, but in a certain relation to, that of the catalytic ion.

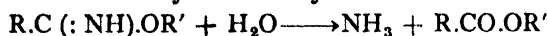
Lapworth's investigations dealt mainly with the accelerating effect of hydrogen chloride in ester formation; the results of a large number of measurements led him to the view that free hydrogen ions are the essential catalysts, and that the presence of water is anti-catalytic owing to the free ions being rendered inert by conversion into hydrated ions. The "availability" of an acid in catalytic esterification was thus



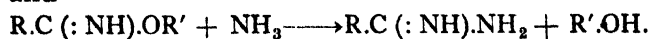
considered as a factor which depends on the relative amount of complex ions formed by association of the hydrogen ions with compounds of a "basic" type—alcohols may be regarded as exceedingly weakly basic, whilst by comparison water is definitely more basic.

These conclusions may be considered jointly with the concurrent work of Goldschmidt<sup>13</sup> and collaborators on the same problem, from which it was deduced that the "active catalyst" is a compound of the interacting alcohol with a free hydrogen ion, and not the latter itself; with Lapworth, Goldschmidt regards the retarding influence of water as due to displacement of the alcohol-ion complexes owing to the formation of hydrated ions.

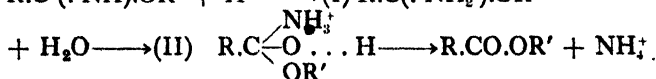
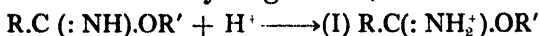
Passing over many investigations conducted on similar quantitative lines and thus amenable to detailed mathematical analysis by these and other workers, reference must be made to the work of Stieglitz<sup>14</sup> and his students upon the interaction of imino-esters with water, ammonia or amines as influenced by the catalytic action of acids:—



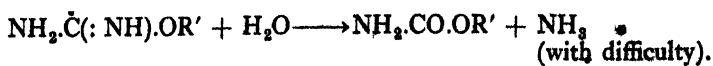
and



This change is very sensitive to, and markedly accelerated by, the presence of traces of strong acids, such as hydrogen chloride, and Stieglitz ascribed the catalysis to the formation of an ionised complex of the ester with free hydrogen ion; thus:—



In other words the catalytic action is due to the alteration of the positive ion of a very weak base (I) into that of a stronger base (II); this theory is strongly supported by its ability to explain apparently conflicting cases. Thus, urea esters are quite stable in acid solution, whilst acylated urea esters are readily hydrolysed:—

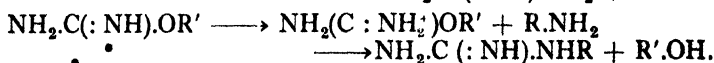
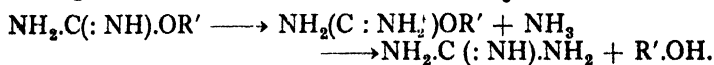


In the case of simple urea esters the positive ion :—

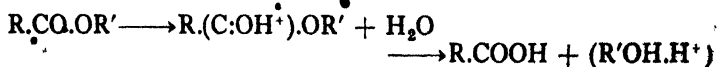


is derived from a stronger base than ammonia, whereas the acylated urea esters are, like the simple imino-esters, weaker bases than ammonia.

On the other hand, acids readily accelerate the action of ammonia or amines upon simple urea esters, and, significantly, the product (a guanidine derivative) is a stronger base than the original urea compound :—



Rideal and Taylor (1926, p. 341) extend Stieglitz's explanation of the catalytic decomposition of imino-compounds to the more general case of ester hydrolysis and esterification, on the principle that the essential action is the conversion (by a hydrogen ion) of a weaker base into a stronger one, and that in the case of esters we have to deal with oxonium bases :—

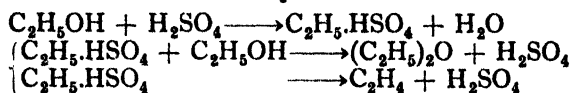


the alcoholic oxonium compound being more basic than the ester oxonium derivative.

All this work is exceedingly suggestive and it will be noticed that, in spite of the somewhat intangible nature of the actual catalytic agent in these cases, the trend of the conclusions is definitely away from the older, cruder view that a free hydrogen ion or hydroxyl ion is the sole explanation of catalytic hydrolysis or esterification, and in favour of (a) an association or "intermediate complex" between the catalyst ion and one or more of the interactants and (b) of an electrochemical mechanism of the changes induced.

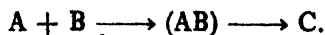
The electrochemical, or electrical, aspect of these changes has received much further emphasis from the investigations of Lapworth, Lowry<sup>15</sup> and others on the question of polarity—the effect on reactivity of a particular group of atoms due to its changed electrical charge, owing to the introduction, elsewhere in the molecule, of a polar atom or radical. This affords a basis for various tentative mechanisms to account for the observed facts in different cases of esterification and hydrolysis.

Parenthetically, the reader may be reminded at this point that the more drastic processes of catalytic dehydration, whereby an alcohol is converted into ether or olefine by means of a mineral acid, have been recognised since the time of Williamson as conditioned by the intermediate formation of definite chemical compounds with the catalyst :—



Leaving the more definitely experimental or kinetic investigations, of which an outline has now been given, some reference may be made in concluding this chapter to recent study of homogeneous catalysis from the standpoint of thermodynamics.

W. C. M. Lewis<sup>16</sup> and others have suggested that thermodynamic or “active” concentrations of the compounds taking part in a reaction should be employed in place of the total concentrations (as used by the older physical chemists) and on this basis Brönsted<sup>17</sup> has deduced that in general any bimolecular action must proceed by the formation of an unstable intermediate complex which then undergoes rapid decomposition :—



The general opinion of workers on homogeneous catalysis, in fact, appears at present to favour the view that in all cases some sort of complex-formation between

catalyst and interactants takes place ; but it must be observed that the precise kind of " intermediate complex " supposed to be present by different workers on different actions takes several forms and is in most cases less defined in nature, and also less definitely substantiated at present by experimental observation, than even the adsorption phenomena established by investigators on catalysis at a solid surface. It may be said, however, that the existence of complexes during aqueous hydrolysis of esters and carbohydrates in presence of acids appears to have been definitely proved by the physico-chemical researches of Kendall.<sup>18</sup>

The question of the energy changes<sup>19</sup> connected with the power of a catalyst to effect a chemical reaction was considered from a general point of view many years ago by Arrhenius, who postulated that molecules do not normally possess sufficient energy to enable them to react, but that, in order to enter into a chemical reaction, a molecule must be " activated," *i.e.*, receive sufficient additional energy to convert it into the reactive state. This energy, measured in terms of heat-energy, is known as the heat of activation (*A*) and may be determined in particular cases from observations of the temperature coefficient of the reaction. Hinshelwood and Hughes<sup>20</sup> find that the value of *A* is constant when taken as the excess energy the active molecules must have, over the average energy of all the molecules, in order for reaction to occur, and that, in the case of three decompositions (those of nitrous oxide, chlorine monoxide, and hydrogen iodide), closely concordant values of *A* are obtained from temperature coefficient measurements and by calculation on the hypothesis of molecular collisions preceding reaction. Further, the absolute temperatures at which each of these actions proceed at the same rate are in direct proportion to the heats of activation obtained, a result which, in Hinshelwood's opinion, is the strongest and principal

evidence for the reality of the "energy of activation"  $A$ .

Catalysis might therefore be regarded merely as the supply of sufficient energy to produce activated molecules, although this does not by any means explain where or how the catalyst acquires the necessary energy for transference to the interacting molecules. It is, however, generally admitted that a catalyst, from the fundamental standpoint, must have other functions than simple activation, since reaction-velocity appears to be controlled, not only by the rate of supply of energy of activation, but also by another factor or factors corresponding to the probability of reaction after activation.

The latter factor might consist merely of the probability of molecular impact by collision, or of a suitable orientation of the reacting molecules or some specifically suitable internal phase relationship of the molecule. In the latter connection attention is obviously directed to the electronic configuration or polarity of the molecule: Hinshelwood points out that if a molecule  $A - B$  receives an impact at  $B$  which directs it away from  $A$ , the small inertia of  $A$  enables it to follow  $B$  with little strain, unless  $A$  were firmly held at a surface, when  $A$  and  $B$  might be forced into a state of strain resulting in disruption. The same reasoning would conceivably apply in a case in which  $A$  was not held at a surface, but had become attached to an electrically-charged particle, with resulting change in the electrostatic conditions existing between the intramolecular groups  $A$  and  $B$ .

Such molecular distortion can be postulated, indeed, either on electrical or other grounds; and in the case of adsorption in a heterogeneous system the results of Palmer and Constable,<sup>21</sup> and of Burk,<sup>22</sup> suggest to the latter worker that adsorption forces can only detach atoms from molecular union if the molecule is adsorbed at more than one point by more than one atom of catalyst. This view, of "multiple adsorption,"

is not opposed to the more general theory of heterogeneous actions as presented in Chapter II and might, indeed, ultimately afford a more lucid explanation of such phenomena as selective hydrogenation and the highly selective action of enzymes.

It will be gathered from the present chapter that much theoretical knowledge still remains to be gleaned with reference to catalysis in homogeneous systems; but it is hoped that the outline which space has permitted will afford a general survey of the field to the reader, who is presumed to be mainly interested in catalysis for its more practical applications in industrial processes.



## SECTION II

### CATALYSES AT SURFACES OF SOLID INORGANIC MATERIALS

#### CHAPTER I

##### A GENERAL REVIEW OF TECHNICAL HETEROGENEOUS CATALYTIC ACTIONS AND THE VARIOUS FORMS IN WHICH CATALYST MATERIALS ARE USED IN INDUSTRY

So far as extent of output and importance of the products are concerned, industrial processes in which gases or liquids, or gas and liquid, are made to interact at the surface of a solid contact agent form by far the most numerous and important group of catalytic methods in technical use at the present time. This will be realised if one reflects that in this way, for example, hydrogen is produced on a scale of many million cubic feet per day—sufficient to supply light and heat to many large cities; ammonia is manufactured from nitrogen and hydrogen in various parts of the world to an extent which is in the region of 500,000 tons of fixed nitrogen yearly; nitric acid is made from ammonia with a smaller, but still relatively large, production; sulphuric acid output in Britain normally approaches 1,000,000 tons annually, about three-quarters being produced by the chamber process with gaseous oxides of nitrogen as catalyst, whilst the contact processes, using platinum or vanadium oxide as contact agent, supply the balance; and, until comparatively recently, chlorine was manufactured by contact processes to the extent of about 50,000 tons each year in this country alone.

The treatment of gases by catalytic agents does not end here; the purification of coal-gas from hydrogen



sulphide and other sulphur compounds is carried out almost entirely by processes which are fundamentally contact actions at solid surfaces. In addition to this relatively long-established process, we have in quite another direction the new methods of union of carbon monoxide and hydrogen to produce methyl alcohol, or (by using different types of contact agent) new types of synthetic fuel. Moreover, motor spirit is now made on an increasing scale from coal, tar oils or heavy crude petroleum residues as raw materials, by the catalytic process known technically as "hydrogenation-cracking."

Again, formaldehyde, the important antiseptic and organic "intermediate," has long been made technically by the combination of methyl alcohol vapour and oxygen at the surface of heated copper, whilst recent work is opening up a wide field in the controlled oxidation of many organic compounds in the vapour state by means of air in contact with certain oxides, usually those of vanadium or molybdenum. The annual output of these and some other organic compounds, produced in this way by interaction of gases or vapours in presence of appropriate solid catalysts, is, of course, much smaller in the aggregate than those of the fundamental "heavy chemicals" first referred to, but nevertheless represents an important and increasing proportion of manufactured organic chemicals.

Turning to the aspect of heterogeneous catalysis in which chemical action occurs in the liquid phase in presence of a solid catalyst, the most important technical application (other than the hydrogenation of coal) is in the case of hydrogenation processes, where hydrogen is made to unite with unsaturated liquid organic compounds of various types by the action of such metals as nickel or palladium, usually the former. The chief application of this method is the hardening or partial saturation with hydrogen of liquid fatty oils; fat-hydrogenation installations at present erected

are probably capable of dealing with an annual world production of at least 500,000 to 600,000 tons of hydrogenated fats. By employing higher pressures and temperatures, and with suitable modification of the catalyst used, fats and fatty acids are now converted on a large scale into the corresponding fatty alcohols. Another important aspect of this method is the conversion of naphthalene, phenols or cresols into hydro-aromatic liquid compounds of value in the paint and soap industries, and as solvents ; whilst hydrogenation in the liquid state is also employed in the production of certain fine chemicals, perfumes, etc., such as menthol and isopropyl alcohol. Although not usually taken into account from this general point of view it should also be borne in mind that many organic synthetic processes, in which copper or other metal is a catalyst causing condensation of two molecules by removal of hydrogen chloride or other compound, are essentially instances of the technical use of heterogeneous catalysis of liquids by a solid contact agent.

The industrial methods which are to be dealt with in this section are consequently characterised by heterogeneity, not only from the standpoint of physical state, but also in regard to the widely varied kinds of materials manufactured and to the differences in working conditions and other factors which will be encountered. As already indicated, the plan adopted is primarily to group the processes according to the physical states present, commencing with gaseous actions at solid surfaces and proceeding to those cases in which the process is carried out in the liquid state in presence of a solid catalyst, one of the interactants usually, however, being a gas. This system lends itself to the separate treatment, in the first place, of water-gas catalyses (production of hydrogen, methyl alcohol, etc.), followed by that of ammonia, nitric acid, sulphuric acid and chlorine.

It is not convenient, however, to adhere too rigidly to this physical system ; and we have found it desirable, for example, to deal with all the processes for manu-

facturing hydrocarbon oils for internal combustion engines in one place. Therefore, although it includes both liquid- and vapour-phase processes, the chapter on hydrogenation of coal and similar materials follows immediately after that in which the production of motor spirit from water-gas has been considered.

Again, in order to render the subject of sulphuric acid manufacture more compact, an account of the chamber process (in which a gaseous catalyst is used and where the acting system is practically homogeneous) is interpolated after dealing with the contact process. The sulphuric-acid chamber process in its original form is one of the rare cases of a homogeneous catalytic action in the vapour phase, and, if the system of treatment were carried to a logical extreme, should be placed in a separate section following the subject of homogeneous catalysis in liquid systems.

There follow two chapters dealing with other gaseous processes effected at the surfaces either of metals or metallic oxides; the industrial applications embraced in this group are diversified, but it may be remarked that, so far as the manufacture of organic derivatives goes, the processes which have been developed are for the most part based upon the original academic investigations of Sabatier and his co-workers.

The various technical processes of catalytic treatment of liquid organic compounds in presence of reduced metals remain to be considered, and the section is concluded with a short chapter on the use of activated carbon *per se* as a catalyst in various reactions.

The general principles governing catalytic action in a heterogeneous system, so far as they are at present understood, have received attention in Section I., Chapter II, and it will be remembered that these may be summarised as follows:—

1. The possibility of achieving a desired chemical interaction at all depends ultimately on fundamental atomic or molecular properties and relationships which are not fully explained; considerable information can,

however, be obtained (if adequate specific data are available) from thermodynamics and the use of the Nernst heat theorem. The theoretical principles at hand are not numerous, and in many cases at present their application to particular cases is difficult or unsatisfactory owing to lack of adequate determinations of various thermal and other constants ; in our opinion the time has by no means yet arrived to give up what may appear to be more or less empirical experimental trials in favour of implicit reliance on theoretical deductions.

2. A desired chemical change, if feasible, may proceed at too slow a rate for practical purposes, or not at all (*i.e.*, with infinite slowness). In many cases, however, the process will operate at a practical speed in presence of a catalyst.

3. In the case of solid catalysts acting on liquids or gases, the essential conditions for development of catalytic activity are :—

(i.) the presence of a surface as extended as possible, in order to give maximum mechanical contact with the gaseous or liquid phases, and characterised by an irregular structure, apparently to such an extent that a perceptible proportion of the component atoms or molecules is, as it were, exposed so that part of the chemical affinity of the atom (or molecule) in question is not satisfied by the mutual attraction of neighbouring atoms (as is the case in a smooth solid surface) ;

(ii.) the presence at such a surface, whether constituting the latter *per se* or deposited upon it, of a specific chemical capable of bringing about the desired interaction.

The chief distinction between an industrial catalytic process and any other technical method, so far as the actual catalyst is concerned, lies in the care which must be taken to produce the specific active surface in the first place, and then to ensure that this surface is not materially altered under working conditions, either by exposure to too high a temperature, or by adsorption of or combination with traces of other substances

which, by preventing contact between the solid surface and the interactants, act as "catalyst poisons" (*cf.* Section I., Chapter II, p. 31).

The conditions of catalyst production for any given technical process must be considered from the standpoint of the particular case. It frequently happens, for example, that the most highly active form of catalyst is not suited to a works process because it is impossible to prevent a rapid decline of activity under working conditions; if the material forming the catalyst is abundant and relatively cheap, it is often more economical to employ a much larger quantity of catalytic agent of mediocre but prolonged activity than a special preparation of high activity, short life, and expensive to produce from the cheaper, often naturally-occurring, forms.

A good example of this is afforded by the reduced iron catalysts employed in the catalytic production of hydrogen from water-gas, or of ammonia from nitrogen and hydrogen. These are probably in many cases suitable forms of hydrated oxide of iron ores, broken to a convenient size, possibly treated with additional "promoter" substances, carefully dried and reduced without undue exposure to high temperatures (*e.g.*, not above  $500^{\circ}$ – $600^{\circ}$ ). In other words, there is nothing to be gained by producing a catalyst surface which cannot exist unchanged at the necessary reaction-temperature. It will thus be seen that a catalyst of maximum economic efficiency and one of maximum possible activity are not necessarily synonymous terms.

Again, the practice of employing catalysts for vapour-phase work in the form of moulded pellets has become very usual in a number of present-day processes. The powdered material, suitably prepared by precipitation or otherwise, is pressed by machines into small cylindrical pellets (a trace of suitable cohesive substance being added before pelleting in some cases in order to give coherence to the compressed mass). In such catalysts utilisation of all the catalytic

substance present is of course far from attained, but this is more than compensated for by the ease of passage of the gases between the packed pellets, the exterior of the latter forming the effective surfaces of contact action.

Typical cases, in which natural ores or substances obtained by simple treatment of cheap existing materials form the basis of technical processes, include not only the use of treated or untreated oxides of iron in hydrogen and ammonia manufacture, but also similar catalysts used in the base metal catalytic oxidation of ammonia, and in the first stage of the Mannheim contact sulphuric acid process; in the latter the catalyst consists simply of burnt pyrites taken from the pyrites-burner residues. Similarly, the iron-oxide used in gas-purifiers is simply natural hydrated oxide or basic carbonate of iron, or similar material. In the case of reduced catalysts of this kind, the actual metallic catalyst is, of course, the reduced surface film of metal resting ultimately on a "support" consisting of partially reduced or wholly unreduced oxide.

Another class of catalysts which are not deposited on a "support" of another material consists of metals in a more or less "massive" condition with an irregular surface and, in some cases, a porous or spongy internal structure. The simplest instances of this group are the platinum gauze used in the oxidation of ammonia to nitric oxide, and the copper gauze employed in oxidising methyl alcohol to formaldehyde in a current of air. It is well known that smooth-drawn metals of this type are at first sluggish in their action, but in course of use the continual production of oxide or other compounds at the surface film, followed by continual regeneration of the metal, causes the formation of an irregular, rough surface, which attains a state of maximum and constant activity. Cases in which an elemental catalyst can be directly employed in this manner are not, however, frequent. A modification of the use of originally smooth gauze is that in

which, a mass of fine metal turnings ("metal wool") exposing a considerable area per unit volume, is held in a cage and coated in the first place with an attenuated film of oxide by being made to form the anode of an electrolytic cell, or by immersion in a solution of a hypochlorite; the superficially oxidised mass is washed, dried and reduced. In this way active nickel catalysts are produced technically by means of which fats or other unsaturated liquid organic compounds can be continuously hydrogenated, the heated liquid flowing over the catalyst at a suitable temperature and meeting a current of hydrogen flowing upwards in the opposite direction. For ammonia synthesis it has been proposed to employ iron turnings oxidised electrolytically in a potassium carbonate solution, and reduced without washing (in order to retain alkali in the surface film on account of its "promoting" action on the union of nitrogen and hydrogen; *cf.* this Section, Chapter V, p. 159).

An alternative to the formation of a minute film of active material at the surface of solid metal is to produce the metal by reduction from its oxide in an extremely spongy condition, full of minute capillaries, the surfaces of which are irregular, *i.e.*, in the active state. This can be effected in the case of copper, because fused cuprous oxide is reducible at a temperature so low ( $250^{\circ}$ – $300^{\circ}$ ) that the resulting metal has little or no tendency to sinter. Since the density of copper is greater than that of the oxide, whilst the total volume of the mass does not shrink appreciably, the reduced metal is obtained in the form of a mass of minute interlaced rough-surfaced fibres separated by capillary spaces. The majority of fused oxides, however, are reducible only at a temperature which leads to general shrinkage and sintering of the granules. Some of the iron-alkali catalysts used in ammonia synthesis are obtained by reduction of iron oxides produced by fusion of pure iron in a current of oxygen in presence of an alkali hydroxide.

A somewhat analogous case is that of "activated charcoal," made first of all by incineration of wood fibre in such a way that the product is filled with minute interstitial pores. By further treatment of the product with air and steam at a high temperature the pore-surfaces are "activated," doubtless owing to the irregular structure produced by partial removal of carbon atoms from the original smooth surface.

The chief advantages of the catalyst materials discussed in the preceding paragraphs are ease of production on a technical scale, relative constancy of activity under working conditions, good thermal conductivity, and comparative ease of reactivation when, in course of time, they become spent owing to gradual accumulation of poisons. Deactivated metal turnings, for example, can be brought back to full activity by washing in an appropriate solvent followed by fresh anodic oxidation in an electrolytic cell; carbon, copper, and certain other of these materials are rejuvenated by simply heating them to a high temperature for a short time in air, when toxic impurities are burnt off, and the cooled catalyst (after reduction in the case of a metal) is again obtained in an active condition.

It will be noticed, when the various industrial catalyses are described in fuller detail, that many of the actions in which catalysts of this type are used are exothermic, especially in oxidation processes. The use of a substantially metallic mass is a great advantage here in assisting in the rapid dissipation of the heat of reaction, a matter which is of vital importance in controlling the mean temperature, which must almost always be held within a relatively narrow range to obtain maximum efficiency.

The same principle applies to other exothermic processes in which, however, the actual contact agent is a metallic oxide of relatively poor heat conductivity. Examples of this are the production of acetone from acetic acid in contact with heated alumina, calcium oxide (carbonate), etc., and, especially, the



controlled oxidation of aromatic compounds (*e.g.*, naphthalene or benzene) in presence of oxides of vanadium or molybdenum. Additional heat conductivity is sometimes imparted to the contact mass in such cases by distributing it in the form of a thin paste or adherent film on metallic balls or turnings; for example, the vanadium oxide catalyst is frequently mounted on aluminium granules, or on iron turnings or balls which are completely covered with a coating of aluminium.

Finally, we must consider the numerous varieties of supported catalysts in which the active component is mechanically distributed over the surface of a more or less porous, non-catalytic material in order to expose a maximum amount of active surface. The supports employed, which are usually bad conductors of heat and are chosen chiefly for their resistance to high temperature or their extreme porosity, range from broken brick and pumice through asbestos and similar substances to highly porous or absorptive materials, such as kieselguhr, silica gels, or activated carbon. It is, of course, necessary that any compounds which hinder or "poison" the particular process shall not be present in the support used, whilst it is, on the other hand, advantageous if, *per contra*, the latter contain compounds which act as "promoters" or aids to the main catalyst.

In the oldest types of catalytic process, where mechanical dispersion of the catalyst was the primary aim, firebrick, pumice, porous tile and stone, etc., were freely employed; thus, in the Deacon-Hurter chlorine process, firebrick impregnated with copper chloride was used, and in the earliest forms of contact sulphuric acid manufacture the platinum was deposited on purified pumice, and at a later stage on asbestos. Special fireclay has been used as a support for nickel (impregnated as chloride) in the South Metropolitan process for removal of carbon disulphide, etc., from coal-gas. Special means of producing a voluminous

material have been used from time to time, for example, the platinum-magnesium sulphate catalyst in the Grillo sulphuric acid contact process, or voluminous nickel oxide produced by deflagration of a mixture of nickel nitrate and sugar, starch, etc., with or without additional inert materials.

It is in cases of actions at solid surfaces in a liquid medium that most attention has been paid to the quasi-chemical influence of the porous support employed upon the activity of the catalyst. In processes employing the liquid phase and catalyst in the form of powder, the amount of the latter is reduced to a minimum and may be of the order of 1-0.1 per cent. of the liquid in process. Under these circumstances, high catalytic activity becomes much more important than in continuous processes like most of those quoted in the foregoing review. The choice of support is therefore an important matter, especially since it has been found that porosity or mechanical surface is not the only factor operative, the chemical nature of the support also influencing the activity of the catalyst. The general conditions governing the activity of such catalysts will have been gathered from the information given in Section I., Chapter II (pp. 28, 39), on the question of catalyst promoters, and here it need only be indicated that, according to the specific end in view, charcoal, kieselguhr, silica gel, etc., may in turn be found most efficient; and that, moreover, the presence of suitable (usually minute) proportions of special promoters in the support, in addition to the actual catalyst, is frequently found to enhance the technical efficiency of the latter.

## CHAPTER II

### GENERAL SURVEY OF METHODS OF HYDROGEN PRODUCTION

#### Introductory.

IN a description of those important modern industries which have been developed in the last few years by means of catalytic action at the surface of solid materials, attention should be first directed to the methods available for the production of the hydrogen which serves as a primary material for a very large number of these catalyses. A mixture of hydrogen and nitrogen forms the raw material for the synthesis of ammonia and its derivatives and very large quantities of hydrogen are consumed in the fat hydrogenation industry, the production of solvents from aromatic hydrocarbons and phenol by hydrogenation, and in the modern hydrogenation-cracking process for the production of petrol and other commodities from coal, tars and mineral oils. Hydrogen itself is commonly manufactured nowadays by means of more than one catalytic process, and also by other methods which do not involve catalysis. It has therefore seemed best to devote the present chapter to a review of *all* the processes in technical use for the production of this gas.

The more important methods of hydrogen manufacture in actual use or which have been proposed are as follows :—

(1) From water-gas or similar gases :

(a) By the "catalytic process."

(b) By the Lante, Messerschmitt and Bamag processes.

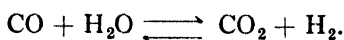
(c) By liquefaction.

(2) From hydrocarbon gases :

- (a) By the catalytic "methane-steam" process.
- (b) By partial combustion with air or oxygen.
- (c) By pyrolysis.
- (3) From water by electrolysis.
- (4) From water by the Bergius process.

### 1. Production of Hydrogen from Water-gas and Similar Gases.

(a) *By the "Catalytic Process."*—Water-gas and producer-gas, which consist mainly of a mixture of carbon monoxide and hydrogen with smaller, varying amounts of nitrogen, carbon dioxide and hydrocarbons, can be converted into hydrogen and carbon dioxide by a catalytic process based on the reaction\* :—

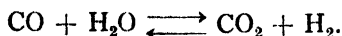


This process gives a larger yield of hydrogen in proportion to water-gas than other methods and has been operated on an enormous scale for the production of hydrogen for ammonia synthesis and for the hydrogenation-cracking of coal. In the former case the composition of the water-gas or producer-gas is adjusted so as to provide a mixture of hydrogen and nitrogen in the correct proportions in the catalysed gas.

The crude hydrogen contains about 2 per cent. of unconverted carbon monoxide, which requires removal by compression through ammoniacal copper solution or otherwise. In the case of high-pressure catalyses such as ammonia synthesis and coal hydrogenation, this is no disadvantage, but in the case of fat hydrogenation and similar processes conducted at atmospheric pressure, the costs of compression must be considered, and the catalytic water-gas process is rarely used in such cases.

The normal source of hydrogen by this method is water-gas from the ordinary blue water-gas producer, made by the action of steam on coke at about 1,200°, and consisting of 45 per cent. or somewhat more of carbon monoxide and of hydrogen, together with minor

amounts of nitrogen, carbon dioxide, methane, etc. Broadly speaking, therefore, water-gas may be regarded as a mixture of equal volumes of carbon monoxide and hydrogen, and it is possible to convert this mixture into carbon dioxide and hydrogen under suitable conditions in accordance with what is known as the water-gas equilibrium :—



It should be added that for some purposes, especially ammonia synthesis, it is possible to employ cheaper forms of gas than water-gas, namely, various forms of what is known as producer-gas. In these cases the incandescent coke is submitted to the action of a mixture of air and steam, with the result that the gases produced consist of a mixture of hydrogen, carbon monoxide, carbon dioxide and nitrogen, the oxygen of the air present having been employed in converting a certain amount of carbon monoxide into dioxide. By suitable adjustment of the temperature of the producer and the proportion of air employed, it is possible to obtain a gas mixture which, after further passage with steam over one of the catalysts to be described, followed by removal of the carbon dioxide present, leaves a mixture of nitrogen and hydrogen in approximately the correct proportions for combination to ammonia. Alternatively, producer-gas and water-gas may be generated separately and subsequently mixed in suitable proportions.

Whilst variations in procedure of this kind may therefore be made to suit the particular nature of the use for which the hydrogen is destined, the principle of the process and also the manner in which it is carried out technically are the same in all cases, and will be understood most readily by a description of the production of hydrogen from ordinary straight water-gas.

The water-gas equilibrium  $\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$  is dependent ultimately on the temperature of

the system, and data are available from the researches of Hahn<sup>1</sup> and Haber for the values of the equilibrium constant " $k$ " derived from the following equation:—

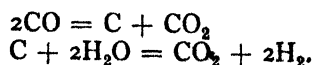
$$k = \frac{p_{\text{H}_2\text{O}} \times p_{\text{CO}}}{p_{\text{H}_2} \times p_{\text{CO}_2}}$$

These are as follows:—

Temperature .	400°	500°	600°	700°	800°
$k$ . . . . .	0.05	0.1	0.3	0.6	0.9

Hence it is evident that in order to obtain maximum conversion of carbon monoxide and steam into hydrogen and carbon dioxide, the equilibrium should be attained at as low a temperature as possible. The rate of attainment of equilibrium is, however, exceedingly slow at the lower temperatures and, if it were not for the fact that certain materials accelerate the change, the water-gas reaction in question would not be of technical interest. It has been known for a long time, however, that iron and related metals of the iron group possess the property of acting as catalysts for this reaction, and these metals have been used technically since about 1913 in the catalytic production of hydrogen from water-gas.

As a matter of fact, Mond and Langer<sup>2</sup> took out a patent in 1888 for the passage of gases containing carbon monoxide and hydrocarbons with excess of steam over heated metal catalysts, such as nickel or cobalt at about 400°, and stated that hydrogen was thereby produced. The view which they took of the mechanism of the action was that the carbon monoxide or hydrocarbons were broken up with production of free carbon, the latter being further attacked by the steam; for example:—



Although, especially at higher temperatures, deposition of carbon on the catalyst itself undoubtedly takes place, it is not believed at present that this plays any great

part in the hydrogen production process ; the latter is at present regarded as the operation of the water-gas equilibrium stated above, effected in practice by simultaneous oxidation of carbon monoxide and reduction of the steam by the metal-metallic oxide system, which is functioning as catalyst in the change.

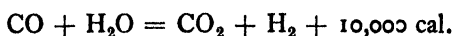
A large number of patents by various groups of workers followed Mond and Langer's original patent in the course of the ensuing twenty years, but no important technical use appears to have been made of any of these until, following the work of Haber and his colleagues, the Badische Anilin und Soda Fabrik<sup>3</sup> took in hand the manufacture of synthetic ammonia (cf. this Section, Chapter V). This company set itself, with characteristic thoroughness, to work out technical means of catalysing the water-gas reaction, and, in a long series of patents, published a whole variety of catalysts, temperatures and pressures by means of which it was said the process could be successfully carried out. In their first patents they emphasised the use of catalysts containing nickel, cobalt, and mixtures of similar metals, but it was evidently soon found that catalysts of this type had too active tendencies towards hydrogenation, with the result that an undue amount of the carbon monoxide present was transformed into methane, which would serve merely as a useless diluent of a gas mixture intended for use in synthesising ammonia. In later patents iron oxide<sup>4</sup> is generally cited as the main component of the catalyst employed, coupled with other substances intended to act as promoters, of which a wide range is given, including oxides of chromium, aluminium, thorium, zinc and many other metals. It is probable that, in technical practice, the catalysts used at the present day consist mainly of a pure form of iron-oxide ore, perhaps stimulated by the addition of small quantities of alumina or similar material, but otherwise untreated and as free as possible from sulphur, phosphorus and similar impurities. In order to maintain a maxi-

imum surface of iron oxide for contact with the gas it is desirable not to heat the ore above  $500^{\circ}$ – $600^{\circ}$  prior to or during its use in the process. The working temperature is usually about  $450^{\circ}$ – $500^{\circ}$ , this being chosen in order to combine rapid reaction with reasonably high conversion to the hydrogen and carbon dioxide side of the equilibrium. By employing excess of steam the equilibrium is moved further over in the direction of hydrogen and carbon dioxide, and in practice, instead of employing two volumes of water-gas and one volume of steam (corresponding to the mixture  $\text{CO} + \text{H}_2\text{O}$ ) it is usual to use about  $2\frac{1}{2}$  volumes of steam per unit volume of water-gas, when the proportion of carbon monoxide left in the finished gas, after passage over the catalyst at  $500^{\circ}$ , is usually found not to exceed 2 per cent.

The equilibrium can also be disturbed in the desired direction by removing the carbon dioxide from the sphere of reaction by means of an absorbent such as lime. The partial pressure of carbon dioxide in the system  $\text{CaCO}_3 - \text{CaO} - \text{CO}_2$  limits the temperature at which this method can be employed to a maximum of  $600^{\circ}$ . It is claimed by Klempt and Brodkorb<sup>5</sup> that the removal of carbon dioxide is a more practicable method of ensuring a good conversion of the carbon monoxide than the use of large excesses of steam. Thus at  $550^{\circ}$ , in order to produce a steam and carbon dioxide-free gas of the same carbon monoxide content as that produced by the passage over lime using one volume of steam, a volume of steam twenty times that of the carbon monoxide would be required. It is claimed that by using a slight excess of steam in conjunction with carbon dioxide removal, carbon monoxide in the final gas is reduced to a trace. In practice,<sup>6</sup> the functions of catalyst and carbon dioxide absorbent can be combined by the use of an iron-containing mineral such as burnt dolomite. The latter can be regenerated by roasting in a specially designed furnace.



The ordinary iron oxide catalytic process is carried out in fairly large units, consisting essentially of an internal catalyst chamber surrounded by flues, arranged in the form of heat exchangers, the temperature of the converter being maintained once the action has started by the heat developed in the reaction, namely,



When starting up a converter a mixture of water-gas and air is first of all burnt in the catalyst chamber in order to raise the temperature of the unit to  $500^\circ$ . A mixture of water-gas and steam in the proportions indicated above is then passed over the catalyst, where it is converted as shown into a mixture of unchanged steam with a gas containing about 65 per cent. hydrogen, 30 per cent. carbon dioxide, 2 per cent. carbon monoxide, and about 3 per cent. of nitrogen, with traces of methane. Owing to the exothermal nature of the reaction the temperature at the exit of the catalyst chamber is somewhat higher than  $500^\circ$ ; the emerging gases are passed through the heat-exchangers, in the other compartments of which fresh water-gas-steam mixture is passing on its way to the catalyst, and is thereby heated up to nearly  $500^\circ$ . The temperature of the emerging gases is thus reduced so that they leave the unit at a temperature not greatly exceeding  $100^\circ$ . The process is therefore continuous and self-heating, and efficient as regards fuel costs and charges for labour.

If water-gas (or other gas mixture) relatively poor in carbon monoxide is being passed into the converter, so that the amount of heat developed per unit volume of gas is considerably less than in the case of a straight water-gas, the temperature of the catalyst is usually maintained by mixing a suitable proportion of air with the entering gases; a certain amount of the carbon monoxide is then burnt directly to carbon dioxide, the heat developed serving to maintain the temperature balance of the system. Owing to the absence of any

external heating the water-gas consumed is practically only that required for the actual chemical action ; it is stated, in fact, that one volume of hydrogen can be produced in practice from 1.1 volumes of water-gas, as compared with one volume of water-gas theoretically necessary. So far as the yield of hydrogen from water-gas is concerned, therefore, this process is far more efficient than any of the intermittent processes described below (*b*), but on the other hand, the cost of the installation, including especially that of the elaborate purification plant necessary, makes the catalytic process suitable only for industries where hydrogen is required on an enormous scale.

In the Badische process for ammonia synthesis discussed in Chapter V, the gas mixture employed is compressed to 220 atmospheres in five stages, namely, from 1 to 3, 3 to 9, 9 to 30, 30 to 90, and 90 to 220 atmospheres. At the Oppau plant of the I. G. Farbenindustrie the mixture of water-gas and steam is passed through the catalyst chambers and then compressed to the 30-atmosphere stage, after which the cooled gases pass through steel cylinders 25-30 feet high and 2-3 feet in diameter, packed with rings, meeting therein a stream of cold water which removes nearly all the carbon dioxide. The aqueous solution of carbon dioxide leaving the base of the towers gives up its internal energy to operate Pelton wheels,<sup>7</sup> whence about 60 per cent. of the energy used to inject the water is recovered. The carbon dioxide evolved is collected in dome-shaped gas-holders about 35 feet high and 35 feet in diameter, which are sealed by stout leather collars lubricated by tar or mineral oil, which trickles down over the exterior of the dome. No water is employed in the storage of the carbon dioxide, which finds use in several ways in succeeding stages of the synthetic ammonia process (*cf.* pp. 163, 169).

The hydrogen is next compressed up to 220 atmospheres, and then passes into somewhat similar

scrubbers containing an ammoniacal solution of cuprous salts, which serves completely to remove carbon monoxide and any carbon dioxide which has escaped absorption in the water scrubbers. The gas leaving the ammoniacal copper scrubbers, if made from straight water-gas, will now contain about 97-98 per cent. of hydrogen, the remainder being almost entirely nitrogen. It should be pointed out that any traces of sulphur compounds present in the original water-gas are completely converted into hydrogen sulphide during the passage over the iron catalyst at 500°, the latter gas being, of course, removed during one or other of the scrubbing processes which follow the conversion.

The ammoniacal copper salt solution is circulated through the system and periodically regenerated by vacuum treatment, which removes all the absorbed carbon monoxide. In order to avoid undue corrosion of the vessels employed to contain the ammoniacal copper solution, it has been found advisable to ensure complete absence of any halogen. Therefore, instead of using the familiar ammoniacal cuprous chloride solution, cuprous formate or cuprous acetate free from traces of halogen is usually employed, and care is taken that a considerable excess of free ammonia is present. It is found that the observance of these conditions makes it possible to employ ordinary steel containers without serious corrosion.

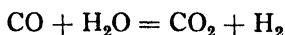
In the Billingham plant of I.C.I., the gases emerging from the catalyst chambers are compressed in two stages, (a) to 50 atmospheres, and (b) from 50 to 250 atmospheres pressure. Carbon dioxide is removed by scrubbing with water at 50 atmospheres pressure, and carbon monoxide by scrubbing through ammoniacal copper formate solution at 250 atmospheres pressure.

In the Standard Oil Co.'s petroleum-hydrogenation plant at Baton Rouge, U.S.A., the carbon dioxide is removed from the reaction gases by scrubbing with triethanolamine in bubble-plate columns at 17 atmo-

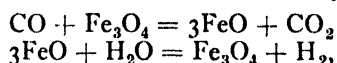
sphetes pressure. The carbon dioxide is stripped from the spent liquor by treatment with steam at atmospheric pressure. For use in petroleum hydrogenation it is not considered necessary to remove the last traces of carbon monoxide from the hydrogen.

### Production of Hydrogen from Water-gas and Similar Gases.

(b) *By the Lane, Messerschmitt and Bamag Processes.* The catalytic process summed up in the equation



may be regarded as the resultant of two simultaneous actions, *e.g.*,



and processes in which these actions were carried out consecutively instead of concurrently were developed, prior to the advent of the catalytic process, for the production of commercial hydrogen for fat-hydrogenation and other purposes. Although these methods involve the consumption of somewhat more water-gas per unit of hydrogen than the catalytic process, the crude hydrogen produced contains less impurity than in the latter case, and may reach a purity of well over 99 per cent. For this reason the processes in question are still in considerable favour with manufacturers of hardened fats.

*The Lane Process.*—This consists in the alternate reduction of iron-oxide ore by water-gas and passage of steam over the reduced oxide, which regenerates iron oxide and sets free hydrogen. In the form advocated in the patents of Lane,<sup>8</sup> the iron oxide, usually small fragments of hydrated spathic or bog iron ore, is packed into retorts about 8 in. in diameter and about 9 ft. in length, a number of these retorts being set horizontally in a brickwork furnace and heated by water-gas firing. The cycle of operations in the plant consists in reducing the ore by pre-heated

water-gas for about 20 minutes, followed by a period of about 10 minutes, when superheated steam is passed over the reduced material. The spent water-gas from the reducing period passes to the heating flues and thence to waste, whilst the first portions of steam and hydrogen from the working period are also rejected in order to eliminate carbon monoxide as completely as possible. The hydrogen produced is passed to a gas-holder after purification, as described below. At its best this process should yield one volume of hydrogen for not more than two volumes of water-gas consumed in reducing the ore and supplying heat.

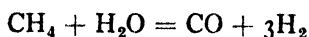
*The Messerschmitt<sup>9</sup> and Bamag<sup>10</sup> Processes.*—A modification of the intermittent iron water-gas process, devised by Messerschmitt<sup>9</sup> and others, has been much employed in Germany, and was adopted by the German authorities as the most efficient mode of producing hydrogen for airships. The retort batteries of the Lane system are replaced by a single vertical furnace of a kiln-like type ("Schachtofen"), which consists of a shaft of annular cross-section containing a large quantity of the broken iron ore with an internal heating flue in the centre and other flues surrounding the shaft externally. The whole furnace is enclosed in firebrick. The cycle of operations is much the same as in the Lane process, and heat is applied by the flues, whilst the charge of ore may be increased in temperature intermittently by burning a mixture of water-gas and air within the furnace itself. It is claimed that this system is more economical to run than the Lane process, and that less water-gas is required to furnish a given volume of hydrogen; the source of economy is mainly the heating system employed, which requires less fuel in the form of water-gas.

Hydrogen prepared by the Lane or Messerschmitt processes will contain only slight traces of sulphur compounds and about 0.2 per cent. at most of carbon monoxide.

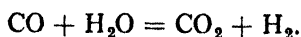
(c) *By Liquefaction.*—Hydrogen may be separated from those constituents of water-gas and coke-oven gas (more particularly methane, carbon monoxide and dioxide) which are relatively liquefiable by passage through a Linde or other liquefaction plant, and it is produced technically by this means in some fat-hardening installations. The gas obtained is, however, by no means free from carbon monoxide.

## 2. The Production of Hydrogen from Hydrocarbon Gases.

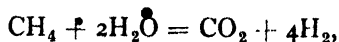
(a) *The Catalytic Methane-Steam Process.*—Methane can be converted into hydrogen by treatment with steam in a two-stage catalytic process. The first stage consists in carrying out the reaction :—



which is the reverse process to that studied by Sabatier,<sup>11</sup> who obtained conversion of carbon monoxide and hydrogen into methane and water in the presence of nickel at 230°–250°. The second stage is essentially the same process as that employed for producing hydrogen from water-gas, namely :—



The overall reaction is thus :—



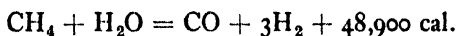
from which it is evident that methane gives rise to the formation of half its weight of hydrogen.

Dieffenbach and Moldenhauer<sup>12</sup> suggested the use of metallic catalysts such as nickel, platinum or similar metals in the form of fine wire gauze to accelerate the first reaction, and the Badische Co. in 1913<sup>13</sup> claimed processes for the passage of a mixture of steam and hydrocarbons over catalysts such as a mixture of magnesia and nickel oxide at about 800°.

The process has been developed on the large scale in recent years by the I. G. in Germany and by the Standard Oil Co. in America. In the latter case plentiful supplies of natural gas and hydrocarbon gases

from the cracking and refining of petroleum are available. In Germany the gaseous hydrocarbons formed during the hydrogenation-cracking of coal and tars are utilised and a substantial proportion of the hydrogen requirements for the process may be derived from this source. Coke-oven gas, which contains about 20 per cent. of methane, has also been extensively employed as a source of hydrogen.

At high temperatures the reaction between methane and steam (the first stage) takes place according to the equation



Calculation of the equilibrium condition shows <sup>14</sup> that at 500° the reaction gas contains CH<sub>4</sub> 33·3 per cent., H<sub>2</sub>O 33·3 per cent., CO 8·3 per cent., H<sub>2</sub> 25·0 per cent., whilst at 940° the composition is CH<sub>4</sub> 0·505 per cent., H<sub>2</sub>O 0·505 per cent., CO 24·8 per cent., H<sub>2</sub> 74·1 per cent. Temperatures in the region of 1,000° are therefore necessary for complete conversion of the methane.

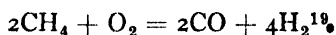
Fischer and Tropsch <sup>15</sup> have investigated the effect of a large number of catalysts on the reaction, and the highest conversions were obtained with catalysts consisting of nickel or cobalt promoted with aluminium oxide and preferably supported on unglazed porcelain. Practically complete conversion of the methane in coke-oven gas was obtained at 860°–930° using the nickel-aluminium catalyst. Marek and Hahn <sup>16</sup> similarly advocate the use of aluminium-promoted nickel, and Hawk, Golden, Storch and Fieldner <sup>17</sup> recommend the use of nickel-corundite and nickel-alundum catalysts which are said to retain their activity over prolonged periods. The process gas should be freed from hydrogen sulphide, which poisons the nickel catalysts by formation of the sulphide. It has been claimed <sup>6</sup> that, by the choice of suitable temperatures and the employment of excess steam, the activity of the catalyst can be maintained in the presence

of small amounts of sulphur, the nickel sulphide being oxidised by the excess steam.

The method is not limited to methane, and the general reaction can be represented as :



The higher hydrocarbons react more readily than methane but exhibit a tendency to deposit carbon on the catalyst. This trouble can be avoided by restricting the composition of the gas and employing an excess of steam. Where a mixture of hydrogen and nitrogen is required for ammonia synthesis the methane-steam reaction is combined with the reaction :



(see below, p. 93), using air as the source of oxygen. In practice either a mixture of air, steam and hydrocarbon gases is passed over the one batch of catalyst or, preferably, a mixture of steam and hydrocarbons is passed through two beds of catalyst in succession, air being introduced at suitable intervals during the passage through the second catalyst bed. By the latter procedure, it is claimed <sup>19</sup> that gases, containing hydrogen and nitrogen in the correct proportions for ammonia synthesis, may be produced, in which the methane content is of the order 0.03–0.09 per cent. In all cases the gases from the process are mixed with a further quantity of steam and treated at a lower temperature (400°–600°) over an iron, or iron-containing dolomite catalyst by the process described on a preceding page (p. 84).

In the Baton Rouge Plant of the Standard Oil Co. of Louisiana, U.S.A.,<sup>20</sup> natural gas containing about 80 per cent. of methane and 17 per cent. of ethane is passed together with 60 per cent. of steam over a catalyst comprising burnt corundite impregnated with nickel nitrate. The catalyst is packed into tubes heated by direct heat in a radiant down-flow furnace to a temperature in the region of 870° and at approximately atmospheric pressure. The exit gases contain



about 69 per cent. hydrogen, 26 per cent. carbon monoxide, 1-2 per cent. carbon dioxide and 1-2 per cent. methane. The second stage is carried out at a temperature of about  $495^{\circ}$  and the final gas contains 78 per cent. hydrogen, 20 per cent. carbon dioxide and 2 per cent. of hydrocarbons and other gases.

(b) *By Partial Combustion with Air or Oxygen.*—Hydrogen can also be produced when gaseous hydrocarbons are burnt in a deficiency of oxygen according to the following reaction :—



- When air is employed for the combustion, nitrogen will be present in the final gas, and the process has only been used to any extent for ammonia synthesis, in localities where the necessary hydrocarbons are readily obtainable (*cf.* above, p. 91). Nitrogen-free hydrogen may be obtained by using oxygen instead of air for the combustion, but the process involves the risk of severe explosions.

(c) *By Pyrolysis.* Gaseous hydrocarbons can be decomposed into their elements by treatment at temperatures in the range  $1,000^{\circ}$ – $1,700^{\circ}$ , the products consisting of a marketable carbon black together with hydrogen of a varying degree of purity. Rose <sup>21</sup> claims that hydrogen of 98 per cent. purity can be obtained by passing natural gas through a furnace packed with refractory material maintained at  $1,650^{\circ}$ . Moore <sup>22</sup> has described the thermatomic gas cracking process of the Thermatomic Carbon Co. of Pittsburg, Pa., as operated for the production of a high-grade carbon black. The process is carried out in a species of water-gas generator filled with chequer brickwork and maintained at a temperature of  $900^{\circ}$ – $1,400^{\circ}$  by alternating blasts of natural gas-air mixture and natural gas alone. The process gas is cooled with water sprays and filtered through cloth bags to remove the carbon black. Natural gas containing 93.8 per cent. of methane gives rise to a gas containing 85.4 per

cent: of hydrogen, 6.3 per cent. of nitrogen, 5.0 per cent. of methane and 1.1 per cent. of carbon monoxide together with traces of carbon dioxide and other gases.

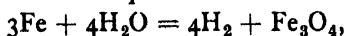
### 3. Production of Hydrogen from Water by Electrolysis.

Hydrogen produced from water by electrolysis is by far the best for catalytic purposes, owing to the absence of any toxic compounds such as traces of sulphur derivatives or carbon monoxide; traces of oxygen, the only possible impurity, are no practical detriment in hydrogenation processes. The cost of production of electrolytic hydrogen in the absence of cheap (water-power) electricity makes its use impracticable in many countries, including England; the large fat-hardening installation of the De-No-Fa Company at Fredrikstad, in Norway, is, however, fed by electrolytic hydrogen, and this source is also utilised in some factories in Italy and in Switzerland both for synthetic ammonia and for fat-hardening. Specially designed batteries of cells for the production of hydrogen are available for catalytic purposes, and in this connection the patented processes of Knowles<sup>23</sup> represent good modern practice. Structural details of electrolytic cells and their mode of operation have been given by Richert.<sup>24</sup> •

### 4. Production of Hydrogen from Water by the Bergius Process.

Mention may be made of the process devised by Bergius<sup>25</sup> for the production of hydrogen by the direct action of liquid water on iron at high temperatures, although this method has not yet found application on the large scale in England. The action is carried out in a vessel capable of withstanding pressures of the order of 500 atmospheres, and consists in charging the vessel with water and suitable iron scrap and heating it to about 300°–350°, preferably in presence of small amounts of ferrous salts and copper. At this temperature and the corresponding pressure

(about 250–300 atmospheres) the action is very rapid, and it is said that as much as 3,000 cub. ft. of hydrogen per day can be obtained from a bomb of ten gallons capacity. The hydrogen is of very high purity and is of course available for use at these high pressures without mechanical compression. The action is simply the usual decomposition :



and silicon, phosphorus or carbon compounds present in the metal remain for the most part unattacked.

It will be clear from the foregoing survey that the method chosen for hydrogen production will depend upon local conditions, such as cost of electric power and availability of the raw material, the degree of purity required by the process for which the hydrogen is intended, and whether or no the said process is to be operated at high pressures.

Bosch <sup>26</sup> gives the average material and energy requirements for the production of 1,000 cub. m. of hydrogen at 0° and 760 mm., subsequently purified and compressed to 200 atmospheres, by several different processes :—

Process.	Requirements.			
	Coke (kg.)	Lignite (50 per cent. water) (kg.)	Fuel Gas (1000 c.h.u. per cub. m.)	Energy (kw.h.)
Coke water-gas, discontinuous	700	—	—	800
Coke water-gas, with oxygen	540	—	—	950
Lignite water-gas, with oxygen	—	1,900	—	1,000
Coke-oven gas, liquefaction	—	—	2,700	1,000
Methane, etc., with steam	—	—	3,200	800
Electrolysis of water	—	—	—	6,300

## References to Section II., Chapter II

### PRODUCTION OF HYDROGEN

#### (1) From Water-gas and similar Gases

##### Catalytic Process

- <sup>1</sup> O. HAHN. *Z. physikal. Chem.*, 1903, **42**, 705 ; 1903, **44**, 513 ; 1904, **48**, 735.



## CHAPTER III

### THE CATALYTIC PRODUCTION OF METHANE, METHYL ALCOHOL AND LIQUID HYDROCARBONS FROM WATER-GAS AND SIMILAR GASES

#### Introductory.

WATER-GAS and other fuel gases such as producer-gas and coke-oven gas, apart from providing the source of the bulk of technical hydrogen, form the basic raw materials for a number of important catalytic processes based on the reactions between carbon monoxide and hydrogen. Most important of these are the production of methyl alcohol and the recently developed Fischer-Tropsch process for the production of liquid fuels and lubricants.

The various processes preferably require gases of a definite composition, but by suitable variations in the water-gas process, by blending water-gas and other fuel gases, and by applications of the "catalytic water-gas" and "methane-steam" processes described in the previous chapter, products containing almost any desired ratio of carbon monoxide to hydrogen may be obtained.

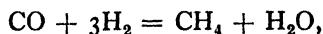
#### The Catalytic Production of Methane from Mixtures of Carbon Monoxide and Hydrogen.

The heat of combustion of methane is considerably greater than that of carbon monoxide or of hydrogen, volume for volume, and many attempts have been made to produce a commercial gas of higher calorific value than blue water-gas by partial or complete conversion of the carbon monoxide present in the latter into methane. For example, the calorific value of mixtures of carbon monoxide and hydrogen does not exceed, as a rule, 300-320 B.T.U. per cubic foot, whereas a mixture of

about 65 per cent. of hydrogen and 35 per cent. of methane has a calorific value of about 500 B.T.U. per cubic foot, whilst that of methane itself is, of course, still higher. A number of processes have been suggested, and in some cases put into large-scale operation, for the technical production of gases rich in methane, but so far they do not appear to have been strikingly successful, presumably because there is insufficient economic demand for gas supplies of this type.

The suggestions which have been made for the conversion of carbon monoxide into methane may be summarised as follows :—

Sabatier,<sup>1</sup> who showed that carbon monoxide could be hydrogenated direct to methane at about 300° according to the equation



attempted to apply this reaction technically, but found that the following practical difficulties stood in the way :—

1. Presence of traces of sulphur in the original gas rapidly poisoned the catalyst.

2. If only the theoretical three volumes of hydrogen per volume of carbon monoxide are employed, a certain proportion of the carbon monoxide is decomposed according to the equation

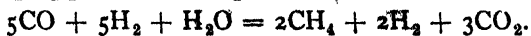


the liberated carbon is deposited on the nickel catalyst and loss of activity results.

3. To reduce the latter difficulty to a minimum it is necessary to work below 300°, and to employ at least five volumes of hydrogen per volume of carbon monoxide. This excess of hydrogen, of course, demands a very large consumption of water-gas per volume of methane finally produced, whilst the latter is inevitably accompanied by excess of unchanged hydrogen.

Sabatier therefore proposed to pass a mixture of water-gas and steam over a nickel catalyst at about 500°, when, to a considerable extent, the process follows the

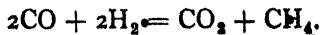
following approximate equation :—



Subsequently, in 1908, Sabatier suggested the use of water-gas prepared at low temperatures (containing a low percentage of carbon monoxide and a high percentage of carbon dioxide) in which the ratio of hydrogen to carbon monoxide was sufficiently great for the direct hydrogenation to proceed smoothly. Carbon dioxide was, first of all, to be removed and the residual gas passed over heated copper to remove sulphur impurities and then over nickel catalyst at about  $300^\circ$ .

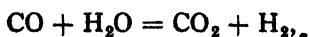
Erdmann and Bedford<sup>2</sup> arrived at a similar result to Sabatier, namely, the employment of a water-gas relatively poor in carbon monoxide and relatively rich in hydrogen, by somewhat different means. They proposed to employ ordinary blue water-gas and to separate it by fractionation at low temperatures (liquid air) into (i) a gaseous portion containing 14–17 per cent. of carbon monoxide and (ii) liquefied carbon monoxide. The carbon monoxide obtained from the liquefied portion was to be employed to drive gas-engines for the liquid-air and water-gas compressors, and also for supplying necessary heat for the catalytic process. The residual gas containing about 15 per cent. of carbon monoxide and over 75 per cent. of hydrogen was found to have been very efficiently purified from sulphur compounds by the liquefaction process, and was suitable for direct passage over nickel at  $280^\circ$ – $300^\circ$ , when a gas was finally obtained containing about 60 per cent. hydrogen, 6–7 per cent. nitrogen and 30–32 per cent. methane, with a calorific value of about 480–490 B.T.U. per cubic foot.

Armstrong and Hilditch<sup>3</sup> have drawn attention to the fact that when purified water-gas alone is passed over nickel at about  $250^\circ$  a considerable amount of change takes place according to the equation

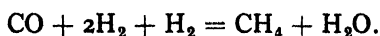


This process is regarded as the result of two consecu-

tive actions, namely, the ordinary "water-gas action"



followed by



Vignon <sup>4</sup> proposed to pass a mixture of water-gas and steam over lime at 800°–900°, the total change again being expressed roughly by the above equation. He subsequently found that the same reactions occurred at a somewhat lower temperature in the actual water-gas producer if a mixture of coke and lime was employed instead of coke alone.

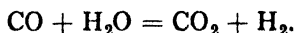
The Sabatier and Erdmann-Bedford processes have been tried out on a moderate scale at various periods in the gas undertakings of one or two small Continental towns. The inherent difficulty in these methods is, of course, the cost of removal of the carbon dioxide produced or, alternatively, of the carbon monoxide to be eliminated in order to provide a suitable mixture of the latter with excess of hydrogen. The thermal advantages of the enriched gas, in other words, are insufficient to bear the necessary charges for gas compression or for lime absorption of the carbon dioxide produced in the Sabatier process.

As a result of the development of coal hydrogenation, sulphur-resisting catalysts have been discovered and attempts have been made to utilise them in the conversion of the carbon monoxide in fuel gases to methane. Meyer and Horn <sup>5</sup> claim that high conversion of carbon monoxide, present in illuminating gas, into methane can be obtained in presence of a molybdenum catalyst at 400°; a pressure of 100 atmospheres is stated to be necessary. However, Sebastian <sup>6</sup> claims good conversion of carbon monoxide to methane at atmospheric pressure, using a silica gel-supported molybdenum sulphide catalyst under conditions in which nickel catalysts become rapidly poisoned.

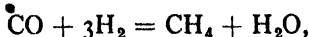


### The Detoxification of Town's Gas.

In recent years the problem of rendering town's gas non-poisonous by the removal of carbon monoxide or by its conversion into harmless products has attracted some attention. Of the possible methods of effecting the removal of carbon monoxide only two have received serious attention, and both of these are catalytic in nature. The first is known as the "single-stage process," and is based on the reaction already discussed:



The other, or "two-stage process," is based on the reduction reaction :



combined with the reaction given above to give the overall reaction :



It is at present generally considered that the single-stage process is the more economic ; the catalyst is cheaper and less sensitive to poisoning by sulphur, and the carbon monoxide can be readily and cheaply reduced to a concentration of 1 per cent. This is considered quite satisfactory, because at such a concentration of carbon monoxide the range of explosiveness of a mixture of the detoxified town's gas and air is reached before that of danger to human health.

The single-stage process is being operated at the present time by the Gesellschaft für Gasentgiftung for the detoxification of the gas supply of Hameln. The process is as follows<sup>7</sup> : the gas, freed from hydrogen sulphide, is humidified by passing through hot-water sprays and at a temperature of 85°-90° enters the heat interchangers, where low-pressure steam is added in the ratio of 10 moles per mole of carbon monoxide. The gas and steam then pass through two reaction chambers in series packed with the catalyst, the heat necessary to maintain the temperature of 450° being supplied electrically or by the catalytic combustion

of a portion of the gas. The gas, after passing through the heat interchangers, is cooled by cold-water sprays, the resulting hot water being used over again in the humidifiers. To avoid necessity for removal of the resulting carbon dioxide, the calorific value of the detoxified gas must be increased by suitable enrichment. In the Müller variation<sup>8</sup> of the "G.f.G." process, the carbon dioxide is removed by water-washing and returned to the coke ovens, where it leads to an increase in the carbon monoxide content of the raw gas.

The experience obtained at the Hameln plant suggests that the process is economic and that further reduction in costs can be effected. At the present time the plant handles 89.36 million cub. m. per annum at an estimated cost of 0.267 pf. per cub. m. (0.9d. per 1,000 cu. ft.).

#### **Removal of Small Proportions of Carbon Monoxide from Gases.**

It is convenient at this point to deal with the removal of small proportions of carbon monoxide from gases in general, and from hydrogen in particular, since it is frequently essential to remove all traces of carbon monoxide as completely as possible from hydrogen which is to be used in hydrogenation processes in which, for example, nickel is employed as catalyst. The removal can be effected in three ways:—

(a) *Scrubbing through Solutions of Ammoniacal Copper Salts under High Pressure.*—When, as in the "catalytic water-gas" and similar processes for manufacturing hydrogen, the crude hydrogen contains 2–3 per cent. of carbon monoxide, and when in any case the hydrogen has to be compressed to more than 100 atmospheres in the course of the subsequent catalytic process, it is most convenient to remove the carbon monoxide completely by scrubbing under pressure through ammoniacal copper formate solution as described in the preceding chapter (p. 87).

(b) *Conversion to Methane at 300° in Presence of Catalytic Nickel.*—When the impurity is present in quantities not exceeding, say, 0.5 per cent., and the hydrogen is not eventually to be compressed to very high pressures, the carbon monoxide may be removed very simply by passage over a suitable nickel catalyst at about 300°. This procedure is, of course, substantially the same as the second stage of the town's gas detoxification process referred to above (p. 101). The methane, produced in equal volume to the carbon monoxide originally present, is quite inert to the ordinary catalysts, and merely acts as a diluent of the hydrogen. With repeated use of the hydrogen, however, the concentration of methane of course mounts up, and the hydrogenating action may be retarded simply in consequence of the lowered concentration of the hydrogen in the gas mixture. Removal of small quantities of carbon monoxide from hydrogen by this process is effected by preheating the gas in a nest of cylindrical tubes to about 300°, and then passing it through a catalyst chamber maintained at the same temperature. The latter may consist of one or more tubular retorts into which has been packed a granular mass such as pumice or small pieces of fire-brick impregnated with a solution of nickel nitrate, which has been previously gently calcined to yield the oxide. The latter is rapidly reduced at 300°, and yields a surface of active nickel which completely converts carbon monoxide at the concentrations mentioned into methane. If the hydrogen has been thoroughly purified from sulphur compounds, etc., the nickel will retain its activity for a very long period; but traces of sulphur compounds in the hydrogen will cause a more or less rapid de-activation of the catalyst, rendering its renewal necessary at more frequent intervals.

(c) *Selective Oxidation of Carbon Monoxide at the Surface of certain mixed Metallic Oxides.*—As an alternative to hydrogenation of the carbon monoxide

(as in (b)), the latter may be oxidised, more or less in preference to hydrogen, by passing the crude hydrogen, mixed with a small, pre-determined proportion of oxygen or air, over certain oxide catalysts at about  $150^{\circ}$ – $200^{\circ}$ . This procedure, in addition to operating at a lower temperature than the hydrogenation action, has the advantages that the oxide catalyst is somewhat less susceptible than nickel to poisoning by sulphur, and that the product, carbon dioxide, is easily removed.

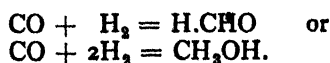
This method was developed more or less independently during the war period by both English and American workers, partly with reference to the technical purification of commercial hydrogen and partly in connection with the manufacture of respirators for dealing with poisonous gases. The work of Harger and Terrey,<sup>9</sup> and of Rideal and Taylor,<sup>10</sup> dealt more particularly with the former problem, and resulted in mixing with commercial hydrogen a small amount of air, sufficient to oxidise from about three to five times the volume of the carbon monoxide present. The mixture is passed over a catalyst which consists of precipitated iron oxide containing about 2.5 per cent. of chromium oxide and about 0.5 per cent. of cerium oxide, at a temperature of  $150^{\circ}$ – $200^{\circ}$ ; the carbon monoxide is much more readily oxidised than the hydrogen under these conditions, and the loss of hydrogen due to simultaneous combustion of the latter is therefore comparatively small. Lamb<sup>11</sup> and his co-workers in America devised a catalyst consisting of 60 per cent. manganese oxide and 40 per cent. copper oxide (termed Hopcalite), and found that this acted as an efficient oxidant for carbon monoxide present in small concentration in air at the ordinary temperature. A gas respirator charged, for example, with Hopcalite, was found to offer useful protection against atmospheric air contaminated with carbon monoxide. They subsequently showed that the same catalyst was effective at temperatures not exceeding

100° for the removal of carbon monoxide from hydrogen, the crude hydrogen being mixed with a small determined percentage of air, as in the Harger process, and passed over the mixed copper-manganese oxide catalyst.

#### The Production of Methyl Alcohol from Water-gas.

Until very recently the only source of methyl alcohol was the distillation of wood residues, the aqueous distillate from which contains a certain amount of methyl alcohol, acetone, and acetic and other acids. After neutralisation of the aqueous liquor with lime the methyl alcohol and acetone are removed by fractional distillation and subjected to further purification. The usual price for wood spirit ("wood naphtha") is about 3s. per gallon, and methyl alcohol is in fairly high demand as raw material for methylation purposes in the dyestuffs and fine chemical industries, and also, at present, as the only source of formaldehyde, which again is required in large quantities for dyestuffs, artificial resins (by condensation with phenol or urea), fine chemicals (including drugs), and as a disinfectant and antiseptic. Furthermore, the market for home-produced motor fuel can absorb large quantities of cheap methyl alcohol, which is of particular value for increasing the anti-knock properties of motor spirit, its blending value in this connection being twice that of benzol.

It has, of course, been obvious ever since Sabatier showed that carbon monoxide can be hydrogenated quantitatively into methane, that a partial hydrogenation which could be arrested at either of the stages indicated by the equations



would be of extreme commercial importance. Many attempts have been made to effect a partial hydrogenation of this kind in presence of nickel, copper, and other hydrogenating catalysts, but it has invariably been

found that the action either does not take place at all or proceeds almost completely to methane without production of anything more than traces of the desired intermediate products.

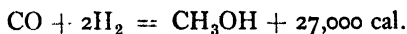
On the other hand, in 1913, the Badische Anilin und Soda Fabrik<sup>12</sup> claimed that in presence of a wide variety of catalysts, notably metals of the iron group with alkalis, zinc, zinc oxide, and other materials, ordinary water-gas was converted, at about 400° and a pressure of over 100 atmospheres, into a complex mixture of hydrocarbons, alcohols, aldehydes and ketones, amongst which methyl alcohol was prominent. No further progress appears to have been made in this direction, however, until about 1923, when Patart,<sup>13</sup> in France, stated that at high pressures and a temperature of about 400°, good yields of methyl alcohol were obtainable by passage of a mixture of water-gas and hydrogen, containing one volume of carbon monoxide to two volumes of hydrogen, over a catalyst consisting of zinc oxide. At about the same time the Badische chemists appear to have returned to the attack and from this date onwards a number of patents appeared, both by Patart and by the Badische Company, claiming the production of methyl alcohol from water-gas employing catalysts which consisted mainly of zinc oxide.

It has been stated that methyl alcohol can be produced by this process at a selling price of 1s. to 1s. 3d. per gallon, thus allowing ample margin for competition with wood spirit. Manufacture of methyl alcohol by this process was commenced at Leuna by the I.G. in 1925, and the estimated capacity of the plant at the present time is 100 tons per day. Production, however, has never reached this figure but has averaged 20,000–25,000 tons per annum. The Billingham plant of I.C.I. has an annual capacity of 20,000 tons of methanol, but during 1934 and 1935 the production was respectively 8,653 and 9,657 tons. The Du Pont Ammonia Co. of America produced 6,000 tons of

## PRODUCTION OF METHYL ALCOHOL 107

synthetic methanol during 1927, and in 1933 the total production for the U.S.A. approximated to 30,000 tons. Synthetic methanol plants are also in operation in France, Belgium, Italy and Japan. It has been stated recently <sup>14</sup> that Duffields Coal Products Ltd. intend to produce methanol from water-gas for blending with motor fuel. The cost of production is estimated at  $2\frac{1}{2}d.$  to  $3\frac{1}{2}d.$  per gallon based on a yield of 140 gallons per ton of coal used.

Thermodynamical considerations show that the reaction



will be favoured by the use of low temperatures and high pressures. A considerable amount of work has been published<sup>15, 16</sup> in the last few years dealing with the equilibrium in the above system, but there has been some disagreement between the results of different workers. The results of Audibert and Raineau <sup>16</sup> are said <sup>17</sup> to be in closest agreement with experimental results and are generally considered to be the most satisfactory. The values of K at three temperatures are given below, where  $K = \frac{\text{CH}_3\text{OH}}{\text{CO} \cdot (\text{H}_2)^2}$  (Audibert)

300°.	.	.	.	K = 2.65 × 10 <sup>7</sup>
400°.	.	.	.	K = 1.15 × 10 <sup>2</sup>
500°.	.	.	.	K = 5.75 × 10 <sup>-2</sup>

The technical feasibility of carrying out the process at temperatures in the range 300°–400° depends on the availability of a catalyst which will promote the change efficiently at these temperatures. The use of iron-alkali catalyst induces combination of carbon monoxide and hydrogen, it is true, but, as will be shown in the final part of this chapter, these conditions tend towards the production of condensation products containing more than one atom of carbon per molecule. Patart appears to have been the first definitely to notice that zinc oxide produced methyl alcohol in good yield with a minimum of the higher by-products, so long as

the temperature was not allowed to exceed about  $400^{\circ}$ .

Subsequent work by Patart, the Badische Co.<sup>18</sup> and Synthetic Ammonia and Nitrates<sup>19</sup> showed quite clearly that a mixture of zinc oxide and chromium oxide or, for example, a basic zinc chromate, is far more efficient than zinc oxide alone. The work of H. S. Taylor and co-workers,<sup>20</sup> and of Garner and Kingman,<sup>21</sup> on the relative capacities of zinc oxide, zinc chromate and other compounds for adsorbing carbon monoxide, hydrogen and methyl alcohol has made clear the reasons for this. Audibert and Raineau<sup>16</sup> have claimed good results with copper-cerium and copper-beryllium catalysts, but the zinc-chromium combination appears to have been generally adopted in practice. G. T. Morgan and his co-workers,<sup>17</sup> at the Chemical Research Laboratory, Teddington, have carried out extensive studies of the methanol synthesis and conclude that the best results are obtained in the presence of any of the zinc chromates, at a temperature of  $350^{\circ}$ – $400^{\circ}$ , and at a pressure of 200 atmospheres; these conclusions are endorsed by the bulk of similar experimental work. There appears, however, to be an optimum molecular concentration of zinc in the zinc-chromium catalyst at which side reactions are at a minimum. Cryder and Frolich<sup>22</sup> conclude that this optimum is in the region of 75 moles per cent. of zinc, and similarly, an early patent of Synthetic Ammonia and Nitrates Ltd.<sup>23</sup> claims the use of a pelleted catalyst containing 70–80 atomic proportions of zinc to 30–20 atomic proportions of chromium.

The gas used in technical practice should preferably consist of a mixture of two parts of hydrogen and one part of carbon monoxide. According to Patart, ordinary water-gas may be employed, in which case about half the carbon monoxide will be left unconverted and the residual gas will possess an appreciable fuel value. In modern practice, however, it is usual to subject the water-gas to the catalytic hydrogen process



described in the previous chapter in such a manner that about one-third of the carbon monoxide is replaced with hydrogen. Similarly, coke-oven gas can be converted into the desired mixture of carbon monoxide and hydrogen by a suitable combination of the "methane-steam" and "catalytic water-gas" processes.

Before passing the gas to the methanol converters, it is necessary to remove all traces of sulphur compounds and volatile compounds (particularly carbonyls) of iron, nickel and cobalt, which tend to promote undesired side reactions. The I.G. have proposed ~~the use of active charcoal for this purpose.~~<sup>24</sup> Likewise, to prevent the subsequent formation of such compounds, the portions of the plant which come into contact with the gases at elevated temperatures should either be coated with metals which do not form carbonyls or should be constructed of special steels containing a high proportion of tungsten, chromium, manganese, molybdenum or vanadium.<sup>25</sup>

The zinc-chromium catalyst, in pelleted or granular form, is contained in vertical, cylindrical converters similar in general construction to those employed in the hydrogenation-cracking of oils (*cf.* Chapter IV, p. 143) and in ammonia synthesis (*cf.* Chapter V, p. 162). The plant is run at a temperature of  $350^{\circ}$ – $400^{\circ}$  and at 150–250 atmospheres pressure, the temperature being maintained by the exothermic nature of the reaction and by the use of an efficient system of heat interchangers between the treated and untreated gases. The exit gases from the plant are passed under pressure through a condensing system in which nearly all the methyl alcohol is removed, the residue being recovered if necessary by scrubbing through water. Simple distillation of the crude product furnishes pure methyl alcohol.

The zinc oxide-chromium oxide catalysts at present used are said to maintain their activity over prolonged periods, and it is claimed that, on the basis of the water-

gas consumed, one part of methyl alcohol can be obtained from two parts by weight of carbon whilst the yield of methyl alcohol per ton of coal originally used should not be less than 400 kg.

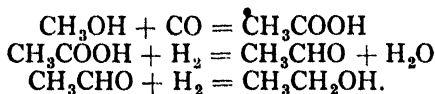
It may be noted that carbon dioxide is similarly reducible to methanol when passed with hydrogen over zinc-chromium oxide catalyst at the same temperatures and pressures as in the case of carbon monoxide-hydrogen mixtures. The consumption of hydrogen would be greater, of course, by this process ( $\text{CO}_2 + 3\text{H}_2 = \text{CH}_3\text{OH} + \text{H}_2\text{O}$ ), but proposals have been made to utilise in this way the carbon dioxide-hydrogen mixture produced during fermentation of starch to butyl alcohol and acetone (*cf.* Section III, Chapter IV, p. 353).

#### Production of Higher Alcohols from Water-gas.

It has been mentioned that the earlier patents of the Badische Anilin und Soda Fabrik<sup>26</sup> in 1913 described the formation of a mixture of liquid hydrocarbons and oxygenated products from water-gas at high pressures and temperatures in presence of iron-alkali catalysts. About 1923 F. Fischer<sup>27</sup> and his collaborators examined this reaction further, with a view to obtaining substitutes for petrol from water-gas. Concurrently, the Interessen-Gemeinschaft,<sup>26</sup> and also Patart<sup>28</sup> in France, appear to have resumed the study of the action of iron-alkali catalyst on water-gas at high temperatures; the object was to obtain, instead of methyl alcohol, either a mixed hydrocarbon-alcohol, etc., product, suitable for fuel for internal combustion engines, or definite technically useful alcohols somewhat higher in the series than methyl alcohol. Higher temperatures ( $400^\circ\text{--}500^\circ$ ) are required than for methanol production, and it would appear that the output from a given plant (essentially similar to that employed for methanol) would be considerably less than when making the latter product.

## PRODUCTION OF HIGHER ALCOHOLS 111

Morgan and his co-workers <sup>29</sup> have studied the effect of adding various alkalis to methanol catalysts and have found that the addition of 15 per cent. of rubidium oxide to a chromium oxide-manganese oxide mixture gave the greatest yields of higher alcohols. The product consisted of methanol 41.5 per cent., ethanol 1.6 per cent., higher alcohols 36.7 per cent., aldehydes, ketones and aldols 15.3 per cent. *Iso*-butanol was the major constituent of the higher alcohol fraction, which also contained *n*-propyl, 2-methyl butyl, 2-methyl amyl, and 2, 4-dimethyl amyl alcohols. The researches of Fischer, which are referred to in greater detail later, ~~suggested~~ that cobalt catalysts have the property of linking carbon atoms, and Taylor <sup>30</sup> has shown that appreciable quantities of ethyl alcohol can be produced by using a catalyst containing 1 gm. equivalent each of copper oxide and manganese oxide and 0.1 gm. equivalent of cobalt sulphide. At 400° and 200 atmospheres pressure the reaction product comprised: methanol 17 per cent., ethanol 22 per cent., other alcohols 11 per cent., and methane 47 per cent. Various explanations have been put forward to account for the formation of these products from water-gas. Fischer and Tropsch <sup>31</sup> suggested that addition of carbon monoxide to the lower alcohol took place, forming the acid, which by successive reductions, gave rise to the aldehyde and the next higher alcohol:—



The interaction of carbon monoxide and methyl alcohol is known to be favoured under high pressures by the presence of alkalis. Morgan <sup>32</sup> considers that his results, particularly the formation of branched-chain alcohols, can best be explained by a series of aldol condensations with aldehydes. Thus the formation of  $\beta$ -methyl amyl alcohol from propionaldehyde is effected by the following series of reactions:—



## PRODUCTION OF HIGHER ALCOHOLS 113

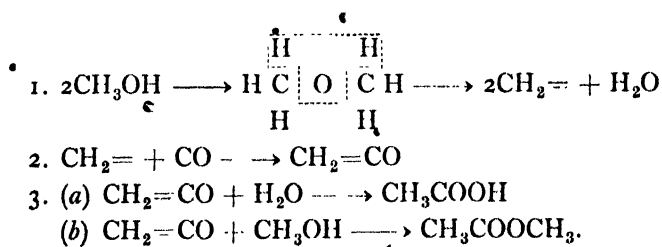
1.  $\text{CH}_3\text{OH} + \text{CH}_3\text{OH} = \text{CH}_3\text{CH}_2\text{OH} + \text{H}_2\text{O}$
2.  $\text{CH}_3\text{OH} + \text{H}\cdot\text{CH}_2\text{CH}_2\text{OH} = \text{CH}_3\text{CH}_2\text{CH}_2\text{OH} + \text{H}_2\text{O}$   
*n*-propanol
3.  $\text{CH}_3\text{OH} + \text{H}\cdot\underset{\text{CH}_3}{\text{CH}}\cdot\text{CH}_2\text{OH} = \text{CH}_3\underset{\text{CH}_3}{\text{CH}}\cdot\text{CH}_2\text{OH} + \text{H}_2\text{O}$   
*iso*-butanol

The technical application of the process appears to be somewhat limited. As operated by the Du Pont Co. of America, it is clearly subordinate to the manufacture of methanol and economically dependent on the sales of the latter product. A patent<sup>35</sup> of the above Company describes the passage of a mixture of 35 per cent. of carbon monoxide and 50 per cent. of hydrogen over a zinc-potassium chromate catalyst at and 250 atmospheres. According to Graves *cit.*) the higher alcohol fraction of the Du Pont product boils over the range 85°-162° and contains 48 per cent. of primary alcohols (main constituents, 2-methyl 1-butanol and 2-methyl 1-pentanol), the rest being saturated secondary alcohols (main constituent, 2, 4-dimethyl 3-pentanol). The process is now only of potential interest for producing technically useful alcohols, the production of "synthol" for motor fuel having been superseded by the atmospheric pressure process of Fischer and Tropsch; and it is doubtful how far it can compete with alternative methods of making higher alcohols, as, for example, butyl alcohol by fermentation of starch, isopropyl alcohol from acetone and the preparation of various alcohols by hydration in the presence of sulphuric acid from the olefines present in natural gas, cracking gases and coke-oven gas.

It is of interest to note, however, that a recent patent to the I. G. Co.<sup>36</sup> claims the production of higher alcohols from water-gas under pressure followed by the dehydration of the alcohols and the polymerisation of the *iso*-olefines thus formed to their dimers and trimers for the manufacture of high anti-knock motor fuels.

### Production of Acetic Acid from Water-gas (Carbon Monoxide and Methanol).

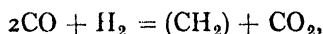
It has already been mentioned that carbon monoxide will combine with alcohols under pressure to form the corresponding acid, and numerous claims have been made in the patent literature for the production of acetic acid and methyl acetate from carbon monoxide and methanol in the presence of catalysts consisting of phosphoric acid or similar non-volatile acids promoted by various metallic elements. Recent work <sup>37</sup> at the Chemical Research Laboratory, Teddington, has shown that under optimum plant conditions, 1.6 kg. of free and combined acetic acid can be produced in 14 hours by passing carbon monoxide and 80 per cent. methyl alcohol over a mixture of 700 gm. of 87 per cent. phosphoric acid with 14 gm. of copper phosphate at 330°-340° and at pressures in the region of 200 atmospheres. The methyl alcohol passing through the plant is accounted for as follows: acetic acid 44.9 per cent., dimethyl ether 9.5 per cent., free carbon 4.8 per cent., unchanged methanol 35.8 per cent., loss 5.0 per cent. The dimethyl ether is considered to be an intermediate product in the following series of reactions:—



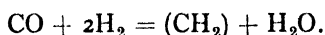
Acetic acid is manufactured at the present time by the oxidation of acetaldehyde, but the patent literature shows that important manufacturers such as the British Celanese Co. and Du Pont are at present much interested in the above alternative process, suggesting the possibility that it may also come to be an important source of acetic acid.

**The Production of Hydrocarbons from Water-gas.**

Attention has already been drawn to the fact that the early "Synthol" products obtained at high pressures contained, in addition to higher alcohols and other oxygenated compounds, small quantities of hydrocarbons. In 1925, F. Fischer and Tropsch<sup>38</sup> made the important discovery that at atmospheric pressure water-gas could be converted into a mixture of liquid and gaseous hydrocarbons, containing only traces of oxygenated compounds, by treatment at  $200^{\circ}$ – $270^{\circ}$  in the presence of catalysts containing iron or cobalt. With an iron catalyst, which operated best at about  $250^{\circ}$ , the reaction was as follows:—



whereas with cobalt, which required a somewhat lower temperature ( $180^{\circ}$ – $200^{\circ}$ ), the reaction proceeded:—



It was found later that nickel catalysts could be made to yield liquid hydrocarbons, but unless the conditions were carefully controlled, methane was the main product.

Probably the most active catalyst yet discovered is Fischer's cobalt-thorium-kieselguhr preparation.<sup>39</sup> This catalyst, prepared by the precipitation of the oxides on kieselguhr followed by reduction in hydrogen, leads to the production of 110 gm. of liquid hydrocarbons per cubic metre of gas treated, falling to 80 per cent. of this figure after 60 days' working. The theoretical yield is estimated to be about 180 gm. per cubic metre.

The falling off in activity of the catalyst is due to the accumulation of adsorbed wax which can amount to as much as 180 per cent. of the weight of the catalyst. Revivification is readily effected by extracting the wax with solvents.

The gas used in the process should preferably contain carbon monoxide and hydrogen in the ratio of 1 : 2, and by carrying out the gasification of coke at

low temperatures, and employing an excess of steam, a gas containing 2 parts carbon monoxide, 4 parts hydrogen and 1 part carbon dioxide can be obtained which is suitable. The carbon dioxide acts merely as an inert diluent. In Germany, the normal discontinuous water-gas process is being abandoned in favour of the continuous gasification of coke, coal or lignite using a mixture of steam and oxygen. Most of the methods used for producing gas for the methanol synthesis can be applied in this case. Fischer recommends a raw material consisting of a mixture of water-gas and "Spalt gas" (the product of subjecting coke-oven gas to the methane-steam process) such that the desired proportions of carbon monoxide and hydrogen are present.

In order to ensure maximum yields of oil, two outstanding precautions must be observed: (1) sulphur, both in the form of hydrogen sulphide and of organic sulphur compounds, must be rigorously excluded from the reacting gases; (2) the reaction temperature must be controlled within narrow limits. If the former condition is not observed, rapid poisoning of the catalyst ensues, and if the reaction temperature is allowed to get out of hand, methane rapidly becomes the main product.

The technical removal of organic sulphur from the gases presented a serious problem in the large scale development of the process. Many contact materials have been suggested for this purpose, notably, a mixture of lead chromate and copper oxide reduced with hydrogen at  $400^{\circ}$  and used at a temperature of  $300^{\circ}$ – $500^{\circ}$ ,<sup>40</sup> and more recently, a mixture of reactive oxides and hydroxides of iron together with at least 10 per cent. of alkali carbonate to be used at a temperature of  $150^{\circ}$ – $300^{\circ}$ .<sup>41</sup> After removal of hydrogen sulphide the gas should contain less than 0.2 gm. of sulphur per 100 cub. m.

Fischer<sup>42</sup> has described the main process somewhat as follows. The gas mixture is saturated with water vapour



and then passed through an oxide purifier to remove hydrogen sulphide. The gas then passes over the heated contact mass for the removal of organic sulphur and thence without cooling to the reaction chambers. Owing to the exothermic nature of the reaction and the need for rigid temperature control, the design of suitable reaction vessels was a matter of some considerable difficulty. The problem was finally solved <sup>43</sup> by the design of a narrow, rectangular unit 20 mm. by 120 cm. in cross-section by 5 m. long, packed with catalyst. The reaction temperature is held closely at 190° and kept constant by the circulation of steam-heated oil round the exterior of the unit, any number of which can be employed according to the desired plant capacity. The heavy oil and water are condensed out by cooling to room temperature and the lighter fractions of the product scrubbed out by the use of active carbon or wash-oil. It has been claimed recently by Fischer <sup>44</sup> that the yields of liquid products can be increased by 10–20 per cent. by carrying out the process in stages and removing the more readily condensible products after each stage. It is advantageous to arrange the rates of passage in the successive stages to compensate for the gas contraction in such a manner that approximately the same volume of gas passes over the same quantity of catalyst. If the different stages are all operated at the same temperature a series of catalysts of successively diminishing activity should be used; if a uniformly active catalyst is used it is preferable to operate the first stage at a somewhat lower temperature than the others. By using a 3-stage system a yield of 141 gm.\* of benzine and oil has been obtained from a gas containing 29.5 per cent. carbon monoxide and 60 per cent. hydrogen (maximum theoretical yield, 185 gm.).

The primary products obtained from a gas containing 29 per cent. carbon monoxide and 58 per cent. hydrogen in the presence of the cobalt catalyst at a temperature of 190° are as follows :—

	Yield (per cent. by weight).	Olefines in fraction (per cent. by volume).
"Gasol," below 30° . . . .	4	50
"Benzine," 30°—200° . . . .	62	30
"Oil," above 200° . . . .	23	10
Soft wax extracted from the oil, m.p. 50°	7	—
Hard wax extracted from the catalyst, m.p. 70°—80° or over . . . .	4	—

These products, called "kogasin" by Fischer, have been found to consist to the extent of 98 per cent. of aliphatic hydrocarbons ranging in complexity from methane to solid paraffins.

The nature of the products is determined by the conditions employed. Thus, increase in the relative concentration of hydrogen increases the proportion of methane, and decrease in hydrogen concentration causes an increase in olefine production. Higher temperatures favour the formation of methane and carbon. Addition of alkalis to the catalyst greatly increases the yield of solid paraffins, and increase in catalyst activity results in higher yields of benzine and correspondingly lower ones of oil.

The benzine or motor spirit fraction of kogasin, being largely paraffinic in nature, has a low anti-knock value (octane number 47–62) and requires the addition of tetraethyl lead or blending with an aromatic spirit before it can be marketed as a motor fuel. The oil fraction, after separation of wax, forms however an excellent Diesel fuel—a paraffinoid constitution being as valuable in a Diesel oil as it is undesirable in a motor spirit. The high-melting waxes are said to be of considerable value in the electrical industries.

In addition to the above uses for the "primary" products of the process, Fischer and his colleagues have worked out conditions for the production of a number of "secondary" products. Thus, the olefines present in the "gasol" fraction may be hydrated by sulphuric acid treatment to produce alcohols. As an

alternative to use as Diesel fuel, the oil fraction\* may be cracked <sup>45</sup> by the methods employed in the petroleum industry to give good yields of high anti-knock motor spirit. Most important of all, however, is the production of lubricating oils,<sup>46</sup> for which purpose three methods have been proposed :—

1. Treatment of the olefine-rich fractions of kogasin with 5 per cent. of aluminium chloride : viscous oils are produced by polymerisation.

2. Higher fractions, low in olefines, are treated with chlorine and one or two chlorine atoms introduced. The mono- or di-chlorokogasin is then subjected to a species of Friedel and Crafts condensation in the presence of aluminium chloride, and chlorine-free viscous oils are produced. The fraction of oil distilling at 125°–250° forms the most suitable raw material for the chlorination process.

3. Viscous oils are obtained by the condensation of the chlorokogasins, prepared as above, with aromatic hydrocarbons such as commercial xylene in the presence of aluminium chloride.

The lubricating oils produced by all these processes are said to be equal to the best petroleum products. Under normal conditions the yields of petrol and lubricating oil (by polymerisation of olefines) are in the ratio of 8 : 1.

The highest yield of olefines (55 per cent.) is obtained when using water-gas containing carbon monoxide and hydrogen in the ratio 1 : 1, in the presence of a cobalt catalyst. Using a nickel catalyst and a carbon monoxide to hydrogen ratio of 1 : 3 only 5 per cent. of olefines are produced. Between these limits various yields of olefines may be obtained.

As a method of producing synthetic petrol from carbonaceous materials, the Fischer-Tropsch process attracted immediate attention, particularly in Western European countries, but its capacity for producing synthetic lubricants is more probably the reason for the widespread interest in the process at the present time ;

for the latter possibility makes it a serious rival to the high-pressure coal and tar hydrogenation processes described in the following chapter.

The cyclic nature of the majority of the products from the coal or tar process makes them fundamentally unsuitable for lubricating oil production, and little success has so far attended efforts to produce a satisfactory lubricant therefrom. The Fischer process is able to achieve this by using, as it were, "single carbon atoms" as the raw material and building up the long chains characteristic of good lubricating oils.

The Fischer-Tropsch process has been tried out by the Ruhr-Chemie A.-G. in a plant producing about 1,000 tons of motor spirit per annum, and proved so satisfactory that it led to the erection of four large plants to be put into operation by four different concerns during the course of 1936.<sup>47</sup> The total projected output of these plants is 170,000 tons of spirit per annum.

It is claimed that the Fischer process is somewhat cheaper to operate than the hydrogenation-cracking process, and this fact, together with the possibilities of its supplying all the requirements of internal combustion engines, namely petrol, Diesel oil and lubricants, places it in the front rank of modern catalytic processes.





## CHAPTER IV

### THE HYDROGENATION-CRACKING OF COAL, TARS AND MINERAL OILS

#### Introductory.

THE expenditure of much time and money on the high-pressure hydrogenation-cracking of coal and coal-tars is due largely to the dependence of the Western European countries on imported petroleum for their supplies of liquid fuel and lubricants. The ever-growing use of these materials necessitates ensuring their adequate supply in time of war, and means have been increasingly sought for their production from indigenous raw materials. Coal is one of the most important of these raw materials, and the catalytic production of methanol, and of motor fuel and lubricants by the Fischer process from coal *viâ* coke and water-gas, has already been described.

In Great Britain a certain amount of motor fuel is available as by-product benzol from gasworks and coke-oven plants, light oil from the Scottish shale-oil industry, and light spirit from the low-temperature carbonisation of coal. Although the amount of motor fuel so produced has been stimulated in recent years by the high duty on imported petrol, the comparative insignificance of such sources of supply at the present time is shown by the following figures :—

	1934      1935 (millions of gallons).	
Total motor spirit consumed . . . . .	1,200	1,260
Motor spirit from gas works, coke ovens and shale-oil works . . . . .	50 1	75
Spirit from low-temperature carbonisation of coal . . . . .		

The carbonisation of coal at low temperatures

(600°–700°) gives a high yield of light tar and a coke suitable for use as a smokeless fuel in domestic grates, and the process in its numerous forms has attracted a great deal of attention in the last ten years or so. From the point of view of motor spirit production, however, it is not a very efficient process; one ton of coal yields on the average  $3\frac{1}{2}$  gallons of light spirit, 16 gallons of tar, 14 cwt. of "semi-coke" and gas. If this "semi-coke" formed the whole of the domestic fuel used in this country, only about 140 million gallons of simultaneously produced low-temperature spirit would be available annually.

The hydrogenation-cracking process, on the other hand, comprises a catalytically-controlled cracking treatment conducted in the presence of excess of hydrogen at temperatures in the range 400°–500°, and at pressures of 200–250 atmospheres. Unlike the cracking processes used in the petroleum industry, coke formation can be entirely suppressed, whatever the nature of the raw material, and gas production minimised. By the hydrogenation-cracking of low-temperature tar a 100 per cent. yield of motor spirit can be obtained, *i.e.*, 16 gallons per ton of coal carbonised. By the direct treatment of coal, a yield of 150–170 gallons per ton can be obtained. Hence it is evident that the treatment of coal itself is the more efficient process for maintaining supplies of motor fuel, although if, as assumed above, the domestic fuel market could be completely saturated by low-temperature coke, hydrogenation of the by-product tar would yield about 700 million gallons of motor spirit per year, or rather more than half the annual requirements.

The hydrogenation of coal, together with such quantities of low-temperature tar and creosote as are available, is being carried out at the present time in this country at Billingham-on-Tees by Imperial Chemical Industries Ltd.\* The plant was completed early in 1935 and by the end of that year was in full production, the annual output of finished petrol being



estimated at 150,000 tons or about 45 million gallons.<sup>1</sup> At the present time the costs of the process are such that without the duty on imported petrol the hydrogenated coal product could not hope to compete with petroleum spirit. There is hope that the large-scale experience now being obtained will lead to material reduction in costs.

In Germany the Leuna plant of the I.G. Company has been operating the process on brown coal and brown-coal tar since 1928 with an annual output of 100,000 tons of petrol.<sup>1</sup> This plant has now been enlarged to produce up to 350,000 tons per year. The Braunkohlenbenzin A.-G. has recently erected two plants (at Doehlen and Magdeburg) each capable of producing 150,000 tons of petrol annually by the hydrogenation-cracking of low-temperature brown-coal tar. Two new plants have also been recently erected for the treatment of bituminous coal, one at the Hibernia Colliery on the Ruhr (Hydrierwerke Scholven A.-G.) to produce 125,000 tons of petrol per annum and the other at Oppau (I.G.) to produce 60,000–70,000 tons per annum. In 1935, Germany produced 320,000 tons of hydrogenated petrol, or 23 per cent. of her annual petrol consumption: the projected output for 1936 is 500,000 tons. Taking into account the 175,000 tons to be produced by the Fischer-Tropsch process, 325,000 tons of benzol and 200,000 tons of power alcohol, home production of motor spirit in Germany during 1936 will amount to 1,200,000 tons, or over 60 per cent. of the total consumption.<sup>2</sup>

In the U.S.A., the Standard Oil Company are employing similar processes to produce petrol from low-grade crude oils and refinery residues, for the production of high-grade lubricants and burning oils and the general refining of many types of petroleum fractions.

#### Historical.

Berthelot<sup>3</sup> in 1868 first attempted the reduction of

coal by heating it in sealed glass tubes with a saturated solution of hydriodic acid at  $270^{\circ}$ . He obtained a 60 per cent. yield of hydrocarbon oil. Development of a high-pressure process, however, is naturally dependent on progress in mechanical and metallurgical science, and it was not until vessels were designed capable of resisting the effects of high pressures and temperatures, that the process under consideration can be said to have been born. The experiments of Ipatiev <sup>4</sup> from 1904 onwards, in which hydrogenation reactions were carried out at pressures up to 100 atmospheres in steel autoclaves, undoubtedly paved the way for the later work on coal and other complex materials. In 1910, Bergius, the acknowledged originator of the process, developed a larger type of high-pressure apparatus in which by treating cellulose and peat in the presence of water at  $340^{\circ}$  and 100 atmospheres pressure a species of artificial coal was produced.<sup>5</sup> Heavy hydrocarbon oils, when treated with hydrogen at 100 atmospheres pressure and at  $450^{\circ}$  in the same apparatus, were found to yield a quantity of light spirit containing saturated hydrocarbons, and the processes involved were patented.<sup>6</sup> Subsequently, Bergius subjected his artificial coal to a similar treatment at  $400^{\circ}$  and obtained a 70 per cent. yield of benzene-soluble oil. Natural coals were found to behave in a similar manner and by 1914 Bergius had succeeded in working out a process for converting German brown coals into hydrocarbon oils.<sup>7</sup> Owing to the intervention of the war in 1914, the process did not reach a technical scale until 1921, when a semi-technical plant was erected at Mannheim-Rheinau.<sup>8, 9</sup> The process was conducted in the liquid phase, and although no catalyst was wittingly employed, a small proportion of Luxmasse (an impure iron oxide), which has since been shown to exert a definite catalytic effect,<sup>10, 11</sup> was added to the reaction mixture to remove sulphur. The products of the original Bergius process consisted of small amounts of petrol together with

phenols, heavy oils, pitch, etc.; the process was not suitable for the production of petrol as the main product.

Credit for the development of the modern hydrogenation-cracking process is mainly due to the I.G. Farbenindustrie A.-G. of Germany, who started work after the war independently of Bergius. The two most outstanding advances made by this company were the division of the process into liquid- and vapour-phase stages and the discovery of active catalysts which were immune from sulphur poisoning. The "key" patents covering these discoveries appeared from 1926 onwards. The first patent citing the compounds of molybdenum as sulphur-resisting catalysts appeared in 1926.<sup>12</sup> German development of the process passed entirely into the hands of the I.G. and the first commercial plant for treating brown coal and brown-coal tar was erected at Leuna in 1927.

The Standard Oil Company of New Jersey signed an agreement with the I.G. in 1927 to operate the process in the U.S.A. with petroleum oils, and in 1929 the first plant was erected at Bayway, N.J. A larger plant was subsequently erected at Baton Rouge, N.J., and was put in commission in 1931.

In Great Britain, Imperial Chemical Industries Ltd. commenced research at Billingham in 1927,<sup>1</sup> and in 1930 announced that a 60 per cent. weight yield of petrol could be obtained from British coals, but that commercial development was possible only with Government assistance. A further hindrance to advance lay in the complex patent position, but in 1931 the way was cleared by the formation of International Hydrogenation Patents Ltd., an association of the I.G. in Germany, the Standard Oil Co. of New Jersey, the Royal Dutch Shell Group and I.C.I., for the pooling of patent rights and the exchange of technical information. In the succeeding years I.C.I. made considerable advances in the application of the process to bituminous coals and, when the British

Hydrocarbon Oils Production Bill was introduced in 1933 and a continued preference on home-produced petrol was thus guaranteed, they proceeded forthwith with the construction of a large-scale coal-hydrogenation plant (*cf.* p. 141).

#### The Hydrogenation-cracking Process.

The conversion of coal or other complex carbonaceous material into low-boiling hydrocarbons entails three obvious changes: a simplification of the molecular structure, an increase in the hydrogen to carbon ratio and the elimination of elements other than carbon and hydrogen. The last two changes can be illustrated by ultimate analyses of the initial and final products:—

	Bituminous coal (dry, ash-free basis).	Petrol.
Carbon, per cent. . . . .	85.7	85.0
Hydrogen, per cent. . . . .	5.5	15.0
Oxygen, nitrogen and sulphur, per cent. .	8.8	—

The optimum conditions for the reactions of cracking and hydrogenation, which together bring about these changes, are fundamentally dissimilar. The cracking reaction is endothermic and is favoured by the use of high temperatures, whereas the hydrogenation reaction is exothermic and favoured by low temperatures. By employing a high pressure, however, a sufficiently high concentration of hydrogen can be maintained to allow hydrogenation to proceed at the temperatures necessary to promote cracking reactions. In practice, temperatures in the range 300°–500° and pressures of 200–250 atmospheres are employed. Under such conditions, hydrogenation reactions will proceed to some extent in the absence of catalysts, but for practical purposes it is necessary to introduce the latter. In view of the nature of the raw materials, the catalyst must be impervious to sulphur poisoning, and it has

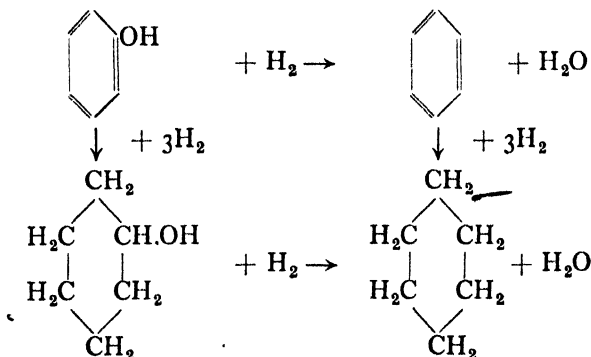
been found that certain compounds which possess low catalytic activity under ordinary conditions are highly active under hydrogenation-cracking conditions, and, moreover, are entirely unaffected by sulphur, carbon monoxide and other catalyst poisons.

The mechanism by which complex materials are converted into low-boiling hydrocarbons can only be elucidated by studies of the behaviour of individual compounds under the conditions employed in the hydrogenation-cracking process. The researches of Kling and Florentin in 1926 led to the first attempt to formulate a general explanation of the destructive hydrogenation of complex substances. From experiments on naphthalene, anthracene and similar compounds<sup>13</sup> they deduced that for every complex molecule there is a limiting temperature at which it begins to disintegrate, this "threshold" temperature coinciding in most cases with the temperature at which the fragments of the original molecule would add on hydrogen. The above experiments, as in the case of most researches on this subject, were carried out in externally heated steel autoclaves or rotating converters of two to five litres' capacity, and the results must only be regarded as being qualitatively applicable to a continuous process.

More recently, a study of the behaviour of typical coal tar constituents in the presence of molybdenum catalysts has been carried out at the Fuel Research Station of the Dept. of Scientific and Industrial Research, and the nature of the main reactions occurring during the hydrogenation-cracking of coal tars has been deduced.<sup>14</sup> From these and similar researches it is possible to classify the reactions involved in the hydrogenation-cracking process as follows :—

1. Compounds containing oxygen, nitrogen and sulphur are converted into hydrocarbons with the production of water, ammonia and hydrogen sulphide respectively. These reactions only proceed to comple-

tion in a reasonable period in the presence of active catalysts such as molybdenum oxide and molybdenum sulphide. For example, phenol,<sup>15</sup> at 450° and 200 atmospheres pressure in the presence of molybdenum oxide supported on active carbon, is converted into a mixture of benzene, cyclohexane and water by the following reactions \* :—



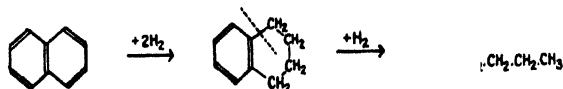
When the hetero atom forms part of the ring system its elimination involves rupture of the ring. Thus, o-diphenylene oxide at 460°–470° in the presence of molybdenum sulphide yields a mixture of benzene, cyclohexane, methyl cyclopentane, phenyl cyclohexane and bicyclic naphthenes.<sup>16</sup>

2. Unsaturated hydrocarbons are hydrogenated to saturated hydrocarbons. Thus, indene is hydrogenated to hydrindene even in the absence of catalysts. Under all conditions the hydrogenation is accompanied by condensation and polymerisation, but in the presence of molybdenum catalysts the polymers are hydrogenated at high temperatures (500°) to oils.<sup>17</sup>

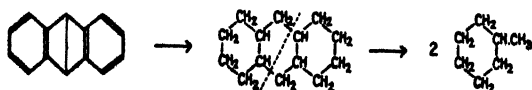
3. Condensed-nuclear aromatic hydrocarbons are converted into benzene, cyclohexane and their homo-

\* Phenol and the cresols can be de-oxygenated to the parent hydrocarbon by treatment with hydrogen at atmospheric pressure in the presence of molybdenum oxide catalysts at temperatures of 350°–450°. Yields of 80–90 per cent. of the theoretical can be obtained. This process is of potential use for the production of toluene from coal-tar cresylic acids. (Cf. Annual Reports of the Fuel Research Board for the years 1930–36; also F. Fischer, T. Bahr and A. J. Petrick, *Brennstoff. Chem.*, 1932, 13, 45.)

logues. This reaction illustrates one of the most important differences between the hydrogenation-cracking process and ordinary thermal cracking. Aromatic hydrocarbons are characterised by a high order of stability to heat treatment and a tendency to react by condensation rather than to suffer rupture of the ring. In the hydrogenation-cracking process hydrogenation of such compounds invariably precedes cracking, and the hydrogenated molecule or portion of the molecule having lost its aromatic structure is then readily cracked. This reaction is well illustrated by the behaviour of naphthalene.<sup>18</sup> At temperatures of  $300^{\circ}$ – $400^{\circ}$ , and an initial hydrogen pressure of 100 atmospheres, naphthalene is readily hydrogenated to tetralin in the presence of an active-carbon-supported molybdenum catalyst. Above  $400^{\circ}$ , the hydrogenated ring opens in the presence of hydrogen forming *n*-butyl benzene :—



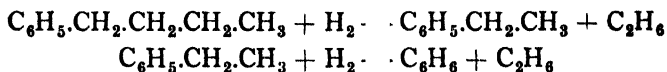
If a large excess of hydrogen or more active catalysts are employed the hydrogenation reaction proceeds further and decahydronaphthalene is produced. This compound is less stable than the tetrahydride and is readily decomposed at temperatures above  $400^{\circ}$ , forming cyclopentane, cyclohexane and their homologues together with gaseous paraffin hydrocarbons. It has been stated,<sup>19</sup> however, that the fully saturated hydride of anthracene cracks without the loss of carbon atoms as gaseous paraffins in the following manner :—



4. Aliphatic and naphthenic hydrocarbons are cracked to form simpler hydrocarbons, addition of hydrogen accompanying or immediately following the

breaking of the carbon linkages. The cracking of hydrogenated rings has already been referred to, but in the case of cyclohexane, ring opening is preceded by isomerisation to methyl cyclopentane, which is then decomposed, forming pentane and gaseous hydrocarbons.<sup>20</sup>

At temperatures above 450° the side chains of aromatic hydrocarbons become shortened and finally removed, as shown by the following examples<sup>18</sup> :—



The higher paraffin hydrocarbons are readily decomposed to the lower homologues. Thus, *n*-octadecane (m.p. 27°) at 490° in the presence of a molybdenum sulphide catalyst yields only 13 per cent. of liquid hydrocarbons (b.p. below 150°), the remainder being converted into gaseous hydrocarbons.<sup>21</sup>

The fully saturated hydrocarbons may be classified in decreasing order of stability as follows : cyclopentanes, cyclohexanes, polycyclic naphthenes, paraffins.

The main function of catalysts in the reactions discussed above is to accelerate hydrogenation, particularly in the elimination of elements other than carbon and hydrogen and in the "pre-hydrogenation" of condensed aromatic structures. In the cracking of saturated compounds it is essential to maintain a rate of hydrogenation at least equal to that of cracking in order to ensure that the "fragments" resulting from the latter reaction are immediately stabilised by addition of hydrogen. It is evident that the success of the hydrogenation-cracking process depends upon a choice of conditions such that a suitable balance is maintained between hydrogenation and cracking reactions. Thus, while it is essential to promote hydrogenation of the condensed aromatic structures and to effect the complete elimination of oxygen, nitrogen and sulphur, it is equally necessary to avoid undue formation of fully hydrogenated hydrocarbons ; the subsequent cracking



of such compounds would lead to excessive gas formation and, moreover, a motor fuel rich in saturated hydrocarbons would possess poor anti-knock properties. Furthermore, with a fixed hydrogen concentration, the temperature at which dehydrogenation is favoured decreases with increase in molecular weight of the compound, and hence conditions favourable to the hydrogenation of the simpler constituents of a raw material would favour dehydrogenation of the more complex constituents. It is usual, therefore, in the case of complex raw materials to conduct the process in stages, suiting the conditions in each stage to the particular change it is desired to effect.

In the treatment of coal the first requisite is the liquefaction of the coal substance and the elimination of inorganic constituents. Bergius has stated <sup>8, 9</sup> that all coals other than anthracites and coals containing more than 85 per cent. of carbon are amenable to treatment, but that the younger coals (*i.e.*, those of higher H/C ratio) are the more readily liquefied. Gordon <sup>1</sup> claims that reduction in ash content by coal-cleaning processes and the use of acid conditions to neutralise the alkalinity of the ash considerably widens the range of coals suitable for the process, and all British coals with the exception of anthracites can be hydrogenated. Much small-scale experimental work has been carried out on the action of hydrogen on coal, in the absence of vehicles, using pure compounds as vehicles, and in the presence and absence of catalysts. The reader is referred to the literature for particulars of this work. <sup>22, 23, 11</sup>

In practice, the original Bergius method of dispersing the powdered coal in a heavy oil "vehicle" (suitably obtained by the conversion of previous batches of coal) is always employed. The vehicle, apart from providing a pumpable mixture, fulfils several important functions: hydrogen is brought into intimate contact with the coal by solution in the oil, the heat of reaction can be dissipated throughout the contents of the

converter and the latter can be stirred by the passage of a stream of hydrogen. Gordon<sup>19</sup> states that maximum yields of oil are obtained with a relatively long time of contact (two hours) and the use of only moderate temperatures. Thus it has been shown that the yield of oil falls from 82 per cent. at 420° to 74 per cent. at 460°, the decrease being accounted for by gas formation. The pressure used is in the region of 250 atmospheres, but the upper limit to pressure is set only by economic and technical considerations.

Catalysts which assist the liquefaction process are incorporated with the coal paste in the powdered form, in solution or deposited from solution on the coal before pasting.<sup>24</sup> This stage can be adjusted to yield either just sufficient heavy oil for pasting purposes (*a*), or an excess of heavy oil to be treated in a subsequent stage (*b*). Typical data for the two methods of operation are given below<sup>25</sup> :—

	Yields, per cent. by weight of A.M.F. coal.	
	( <i>a</i> )	( <i>b</i> )
Petrol . . . . .	31.3	14.0
Middle oil . . . . .	37.3	32.2
Heavy oil . . . . .	5.0	32.2
Gas . . . . .	23.6	15.3
Insoluble organic matter . . . . .	3.0	3.0
Aqueous liquor . . . . .	9.6	9.8
Hydrogen absorbed . . . . .	9.8	6.6

The heavy oil obtained from coal by the above process, coal tars, and heavy petroleum oils are also treated in the liquid phase at moderate temperatures in the presence of small amounts of finely divided catalysts. A static catalyst can only be employed if the raw material is free from asphaltic compounds which would rapidly render such a catalyst inactive.<sup>28</sup>

Most tar distillates, and all middle oils, can be

treated in the vapour phase over a fixed catalyst. To ensure a true vapour-phase reaction, and hence to avoid deterioration of the catalyst, Pier<sup>26</sup> has stated that only oils distilling below 325° should be so treated.

The hydrogen and oil vapour at a pressure of 200–250 atmospheres are passed over a bed of pelleted or supported catalyst at temperatures varying from 450°–520°, depending on the type of product desired. The reaction is exothermic and a large proportion of the heat necessary to maintain the desired reaction temperature is derived from this source. This stage is the main petrol-producing stage and by suitable adjustment of the temperature and type of catalyst, petrols of any desired quality may be obtained. Naphthenic petrols of high volatility are produced at low temperatures with highly active catalysts and aromatic petrols of high anti-knock properties with less active catalysts at high temperatures.<sup>19</sup> From 50 to 70 per cent. of the oil is converted into petrol (end-point 170°), the remainder being re-cycled. The yields for this stage, calculated on the fresh feed introduced, are shown below for the treatment of hydrogenated-coal middle oil.<sup>25</sup>

Petrol, per cent. by weight	:	.	80–93	.
Water	„	„	5	.
Gas	„	„	25–7	.
Hydrogen absorbed	„	.	4.5–6.0	.

#### Catalysts.

In common with other industrial catalytic processes, very little has been published concerning the actual catalysts employed by the companies operating the hydrogenation-cracking process on the technical scale. In the last ten years, however, the patent literature has abounded in specifications covering the use of nearly all the known elements as catalysts for the process. A study of these patents reveals a preference for certain

compounds which is also supported by published experimental work. Compounds of tin can be used as catalysts for the liquefaction of bituminous coal. Horton, King and Williams<sup>27</sup> studied the effect of a number of catalysts on the hydrogenation of a British coal. Luxmasse, which was employed by Bergius in his original process, was found to be more active than pure iron oxide, owing to the presence of titanium oxide in the proportion of one part to ten parts of iron oxide. The most active catalysts were compounds of the elements of sub-group IV (germanium, tin, lead), of which tin was the most active. The use of 0.01 per cent. of stannous hydroxide gave an oil yield equivalent to that obtained in the presence of 2.5 per cent. of iron oxide, and 0.1 per cent. a yield equal to 2.5 per cent. of ammonium molybdate. The function of tin compounds appeared to be the promotion of the initial reaction of hydrogen with the coal substance. Gordon<sup>1</sup> states that I.C.I. concluded in 1929 that tin was the most promising catalyst for the treatment of bituminous coal, and it was planned to employ it in the form of tinned-iron plates arranged as a grid.<sup>28</sup> This arrangement was later discarded in favour of the continuous injection with the coal paste of very small amounts of certain non-volatile organic compounds of tin<sup>29</sup> (*e.g.*, stannous oxalate, formate or acetate) which are decomposed at or below the reaction temperature. Pier<sup>26</sup> recommends that the liquid-phase catalyst should be supported on a finely divided carrier.

The alkaline constituents of the coal ash are said to have a deleterious effect in the liquid-phase treatment of coal,<sup>1, 30</sup> and the use of hydrogen chloride or of compounds which give rise thereto under the reaction conditions effects neutralisation and, in addition, exerts a beneficial effect on the process.<sup>31</sup> In order to make use of this fact it is necessary to devise means of removing the hydrogen chloride from the vaporous reaction products before condensation. I.C.I. has patented<sup>32</sup> a process for preparing a stable suspension

of alkali in oil which can be employed for scrubbing purposes at temperatures in the region of  $450^{\circ}$ . Gordon<sup>1</sup> states that the use of chlorine and tin compounds as catalysts and the discovery of the above means of neutralising the hot vapours were primarily responsible for making the treatment of bituminous coal a sound practical proposition.

The catalyst used in the treatment of oils in the vapour phase is of greater importance than that employed in the initial coal stage, and the bulk of the patented catalysts are intended for use in the vapour phase. The elements most frequently quoted are molybdenum, tungsten, chromium, cobalt, nickel, zinc and magnesium. The oxides and sulphides of molybdenum and tungsten appear to be the most active catalysts. From a study of the effect of over eighty compounds on the hydrogenation-cracking of low-temperature tar, the Fuel Research Board<sup>33</sup> concluded that molybdic oxide in the presence of excess sulphur was the most active catalyst. Reichenbach,<sup>34</sup> in an account of the development of hydrogenation by the I.G., states that (in addition to molybdenum) tungsten and chromium or catalysts containing compounds of these elements are particularly active. Pier<sup>24</sup> states that, as early as 1924, the sulphides of molybdenum and tungsten had been found to be particularly active in the hydrogenation of brown-coal tar.

The sulphides of molybdenum and tungsten appear, primarily, to be active hydrogenating catalysts for use at low temperatures, whereas the oxides of these elements together with other metallic oxides are employed at higher temperatures where aromatic products are desired. Many mixtures of compounds have been patented; details for the preparation of a pelleted catalyst comprising equimolecular amounts of molybdic acid, zinc oxide, and magnesium oxide are given in a recent patent,<sup>35</sup> and the preparation of a hydrogenating catalyst, by subjecting this mixed

catalyst to the action of hydrogen sulphide at  $425^{\circ}$  for 80 hours under a pressure of 10 atmospheres, is covered in a further specification.<sup>36</sup> The activity of molybdic acid when preheated in air and in admixture with zinc and magnesia is also mentioned by Reichenbach.<sup>34</sup>

The mode of preparation and the form of the catalyst are of paramount importance. In the following table are shown some results obtained at the Fuel Research Station<sup>37</sup> for the hydrogenation-cracking of a low-temperature tar in a small-scale vapour-phase plant, at  $480^{\circ}$ , and 200 atmospheres pressure.

Catalyst.	A.	B.	C.	D.
Specific gravity of product . . .	0.850	0.875	0.775	0.856
Yield, per cent. by weight, of fraction distilling below $200^{\circ}$ . . .	39.1	33.8	57.0	37.1

Although under the conditions of the reaction all four catalysts consisted essentially of molybdenum sulphide, the results vary considerably, particularly in the case of catalyst C. Catalyst A consisted of alumina gel impregnated with 25 per cent. of ammonium molybdate, catalyst B, pelleted ammonium thiomolybdate, catalyst D, ammonium thiomolybdate pellets preheated in hydrogen sulphide at  $430^{\circ}$ , and catalyst C, pellets of molybdenum disulphide prepared by adding dilute sulphuric acid to a solution of molybdic acid in ammonium sulphide and heating the resulting precipitate in hydrogen at  $427^{\circ}$ , in accordance with E.P. Provisional Appl. 14593 (1935, Int. Hyd. Patents Ltd.). Furthermore, catalysts A, B and D deteriorated fairly rapidly when treating hydrogenated-tar middle oil (b.p.  $200^{\circ}$ – $300^{\circ}$ ), whereas catalyst C showed no signs of deterioration over the same period of test. A catalyst technically suitable for the vapour-phase process must be mechanically strong and must not deteriorate over a reasonable

period. Deterioration can be brought about partly by the deposition of polymerised products on the catalyst surface, and partly by physical or chemical changes in the catalyst itself. The former appears to be largely a function of the raw material and the latter of the form and mode of preparation of the catalyst.

It has been stated that the vapour-phase catalyst employed in the Standard Oil Co.'s Baton Rouge plant has been in use for a year without suffering deterioration.<sup>38</sup>

### Hydrogen Production.

Hydrogen of a high degree of purity is not essential, and it is usual to employ either hydrocarbon gases or water-gas as the source of supply. In America, where natural gas and petroleum cracking or refinery gases are plentiful, the catalysed interaction of hydrocarbon gases with steam is used for hydrogen production, and even in countries where these materials are not available coke-oven gas provides suitable raw material. Furthermore, the hydrocarbon gases produced in the process itself can be utilised to provide a substantial proportion of the hydrogen requirements. In Great Britain and Germany the experience gained in the manufacture of hydrogen by the catalytic water-gas process for the synthetic ammonia plants provided a ready source of hydrogen for the treatment of coal and tars.

### The Technical Hydrogenation-cracking of Coal and Tars.

*The Bergius Process.*—The original Bergius process which was operated on a semi-industrial scale at Mannheim-Rheinau from 1921–27 is now only of historical interest. The coal-treating plant<sup>8, 9, 39</sup> consisted of three horizontal converters of approximately 55 litres capacity arranged in series and externally heated by gas-fired lead baths. The contents were stirred by mechanically driven stirrers rotating about the central axis of the converters. A

paste of 100 parts of finely powdered coal with 40 parts of heavy oil or tar with which was incorporated 5 per cent. of Luxmasse was pumped through the converters together with hydrogen at 150–200 atmospheres pressure. The temperature in the converters was in the region of 450°. From 1,000 kg. of bituminous coal the following products were obtained :

- 150 kg. neutral refined motor spirit (b.p. 30°–200°).
  - 200 „ “ Diesel ” oil.
  - 140 „ fuel oil.
  - 240 „ coke and ash (after carbonising the sludge from the centrifuge).
  - 5 „ ammonia.
- 50 kg. of hydrogen were absorbed in the process.

*The I.G. Process.*<sup>40</sup>—The coal hydrogenation plant at Leuna, which has recently been enlarged to produce up to 300,000 tons of motor spirit per annum, uses almost exclusively German lignite and low-temperature lignite tar.

Hydrogen is made from water-gas derived partly from lignite by continuous gasification with steam and oxygen in a Winkler producer, and partly from the hydrocarbons resulting from the hydrogenation-cracking process, utilising the methane-steam reaction. When motor spirit is the sole product desired, a two-stage process is used. (1) A paste of the dried, powdered lignite together with catalyst and heavy oil is treated in the liquid phase at 460° and 250 atmospheres pressure to produce spirit, middle oil and just sufficient heavy oil boiling above 325° for pasting-purposes (cf. p. 134). (2) The middle oil resulting from the first stage is treated in the vapour phase over a fixed catalyst at temperatures up to 520° and at 250 atmospheres pressure, and by re-cycling unchanged material, is completely converted into motor spirit. When, however, other products such as fuel oil, Diesel oil or lubricating oil are desired, a three-stage process is



employed.\* The first stage is similar to that described above except that it is operated so as to produce heavy oil as the main product. In the second stage this heavy oil can be treated in the liquid phase to yield products other than motor spirit or to produce middle oil, which can then be subjected to a vapour-phase treatment in a third stage to produce motor spirit. In either case lignite tar can be treated by introducing it as pasting oil in the first stage.

The yield of motor spirit from lignite (55 per cent. by weight) is less than that obtained from bituminous coal owing to its lower carbon content. On the other hand, however, owing to the higher hydrogen/carbon ratio of lignite, the products tend to be richer in hydrogen than those obtained from bituminous coal, and it has only been possible to produce a really satisfactory high-speed Diesel oil when using lignite as raw material.

The plants used for the two types of coal are very similar, and in view of the close collaboration between the I.G. and I.C.I. companies, the Billingham plant for the hydrogenation of bituminous coal may be regarded as typical.

*The I.C.I. Plant at Billingham-on-Tees.*<sup>1</sup>—It is proposed, in future, to produce hydrogen from the hydrocarbons resulting from the hydrogenation process by the action of steam in the presence of catalysts, but at the present time the catalytic water-gas process is employed. Carbon dioxide is removed from the catalysed gas by scrubbing with water at 50 atmospheres pressure and carbon monoxide by scrubbing with copper solution at 250 atmospheres pressure. The hydrogen then passes to the circulating pumps of the coal hydrogenation plant. The coal is cleaned by the Chance process (a "float-and-sink" method employing a suspension of sand in water as the medium) to an ash content of  $2\frac{1}{2}$  per cent. The clean coal

\* I.C.I. has patented<sup>41</sup> the use of a similar three-stage process for the treatment of bituminous coal.

passes to grinding mills *viâ* weighing machines which deliver coal, pasting oil and catalyst in the desired proportions. The mills grind the coal and effect the incorporation of the oil and catalyst. The resulting paste is a fluid and reasonably stable mixture containing approximately 50 per cent. of coal. This paste is fed to hydraulically operated injectors which supply the coal to the converters against a pressure of 250 atmospheres. The coal paste, together with hydrogen, is heated first by the sensible heat of the outgoing products in heat exchangers, and finally in gas-fired preheaters. The final temperature of the reaction mixture entering the converters is of the order of 400°. The mixture passes through three vertical converters arranged in series, entering at the bottom and leaving *viâ* a stand pipe which serves to maintain the desired level of liquid in the vessel. The reaction vessel is a relatively thin-walled container, lined with corrosion-resisting alloy, within the pressure-resisting forging, and insulated therefrom by thermal lagging. The inner vessel withstands the temperatures employed but not the pressures, and the outer vessel *vice versâ*. This arrangement obviates the use of expensive materials in the construction of the heavy forging. The converters, heat exchangers, preheaters and all pipe lines subjected both to high temperatures and pressures are protected from the rest of the plant by a high brick wall, the whole being termed a "stall." Each pair of stalls has a control room containing all instruments and valves for the running of the stalls and for their isolation from the rest of the plant in an emergency. This scheme and also the internal arrangement of the converters has been based largely on the practice in the synthetic ammonia process operated by this company.

On leaving the last converter, the gases and vapours are separated in a "hot catch-pot" from the heavy oil containing ash and unconverted coal. The heavy oil is blown down to atmospheric pressure, the bulk of the heavy oil separated and returned to the pasting mills,

and the residual sludge separated in the sludge recovery plant into coke (which is burnt under the boilers) and a further quantity of heavy oil. The hot gases and vapours are scrubbed with a suspension of alkali in oil to remove hydrochloric acid, and then pass through the heat exchangers and condensers and are finally separated under pressure. The gases are scrubbed with oil under pressure to remove accumulated hydrocarbons and nitrogen, and then pass *viâ* the circulating pumps back into the inlet stream. The liquid products from the "cold catch-pot" or separator are reduced in pressure in three stages, producing a gas rich in hydrocarbons, which is treated for the recovery of petrol, vapours, and gases consisting largely of hydrogen and some gaseous hydrocarbons. The liquid product after separation of ammonia liquor is pumped to the distillation plant, where it is separated into crude liquid-phase petrol (up to  $170^{\circ}$ ), middle oil ( $170^{\circ}$ – $325^{\circ}$ ) and heavy oil (above  $325^{\circ}$ ). The excess of heavy oil over that required for pasting oil is treated in the heavy-oil liquid-phase stalls. The operation of this second stage has not been described in detail, but is presumably similar to that of the first stage. The unconverted heavy oil is re-cycled and the light oil produced separated into liquid-phase petrol and middle oil, the latter being the main product.

The middle oil from both previous stages is then treated in the vapour-phase stalls. These are similar in general design to the liquid-phase stalls, but in this case the preheated vapours of middle oil, together with hydrogen, pass through a bed of fixed catalyst contained in the inner reaction vessel. The liquid product is distilled, the middle oil returned to the converters and the vapour-phase petrol passed to washing plant, where it receives immediate treatment with caustic soda solution to remove hydrogen sulphide. No further refining other than stabilisation to remove propane and butane is required. The liquid-phase petrol, however, requires treatment with strong

sulphuric acid in addition to the soda treatment, and is finally redistilled. The finished petrol comprises a blend of the refined liquid- and vapour-phase products. As already stated, the hydrocarbon gases produced in the process will eventually be used for hydrogen manufacture, but at present the butane is separated, liquefied and sold to the Calor Gas Co. for distribution as a coal-gas substitute in rural districts.

Until the plant has been in operation for a longer period accurate figures for yields will not be available, but the weight yield of petrol on the dry, ash-free coal is stated to be in excess of the earlier quoted figure of 60 per cent. Preparing hydrogen in the present manner from coal *via* coke and water-gas, 500,000 tons of coal are required for the production of the 100,000 tons of petrol made from coal per year. Gordon estimates that if the major requirements of hydrogen were made by the hydrocarbon-steam process, only 3.5—4 tons of coal would be required for the production of a ton of petrol. On this basis the thermal efficiency of the process is 40 per cent. compared with 25 per cent. for electric power generation and 55 per cent. for gasification.

In addition to the 100,000 tons of petrol made from coal per year, a further 50,000 tons are produced by the treatment of low-temperature tar and creosote oil. The tar enters the plant as pasting oil in the coal stalls, and the creosote is distilled *in vacuo*, producing middle oil which passes direct to the vapour-phase stalls and heavy oil which is treated in the heavy-oil liquid-phase stalls. The treatment of these materials, therefore, causes no disturbance of the normal functioning of the coal-treating plant, which can thus absorb as much or as little of such materials as may be available.

#### The Hydrogenation-cracking Process in the Petroleum Industry.

The application of the process to petroleum refining has been developed mainly by the Standard Oil Co.

of America in collaboration with the German I.G.\* In 1930, Haslam and Russell<sup>42</sup> described five major applications of the process, and in a later publication<sup>43</sup> included a sixth :—

1. The improvement of low-grade lubricating oil distillates to obtain high yields of premium quality lubricants.

2. The improvement of off-colour, low-grade burning oils or light gas oils to produce water-white kerosenes of low sulphur content and superior burning properties.

3. The conversion of heavy, sulphurous, asphaltic crude oils and refinery residues into petrol and distillates low in sulphur and free from asphalt, without coke formation.

4. The conversion of paraffinic or aromatic gas oils into stable petrols of low gum and sulphur content and of high anti-knock value, without formation of tar and coke.

5. Desulphurisation and stabilisation of unstable naphthas of high sulphur content.

6. The manufacture of new and specialised products, such as high flash-point "safety" aviation fuels of high anti-knock value and naphthas of high solvent power for use in the lacquer and varnish industries.

These variations of the process are all conducted in the same type of plant with suitable alteration in temperature, pressure, catalyst, etc.

*The Baton Rouge Plant of the Standard Oil Co.*<sup>43</sup>

—Hydrogen is manufactured from natural gas by the methane-steam process described in Chapter II (pp. 90–93) of this Section. The three hydrogen units at Baton Rouge are capable of a combined output of 9 million cubic feet of pure hydrogen per day.

The purified gas (already compressed to 16 atmospheres for the triethanolamine scrubbers) contains over 97 per cent. of hydrogen, and is returned to the compressors and further compressed, up to about 240 atmospheres. This hydrogen, together with re-cycle

gas, is mixed with the oil under treatment (compressed to the same pressure) and delivered to tubular heat interchangers and preheated by the hot reaction products leaving the converters. Additional heat is supplied to the ingoing materials in a gas-fired pipe coil before entering the reaction chambers. The latter, arranged in a vertical position, are 40 ft. high with a reaction space 3 ft. in diameter lined with non-corrosive alloy, and filled with sulphur-resisting catalyst. Three or four of these converters are arranged in series forming a unit.

The reactants enter the reaction chambers at  $370^{\circ}$ – $450^{\circ}$  and the heat of reaction raises the temperature to  $400^{\circ}$ – $540^{\circ}$ , depending on the type of treatment in progress. The reaction products pass from the converters to heat interchangers and condensers, and thence to a high-pressure separator. The residual gas is scrubbed with oil whilst still under pressure to remove gaseous hydrocarbons, is re-compressed in boosters to the working pressure and returned to the system. The liquid products are discharged to a low-pressure separator where dissolved gas is liberated and are then fractionally distilled, the unconverted material being returned to the feed system.

In the treatment of lubricating oils <sup>43</sup> cracking is avoided as far as possible, and by choosing conditions conducive to hydrogenation the elimination of sulphur (and to a less important degree of nitrogen and oxygen) and a general stabilisation is effected. The process is carried out, therefore, at low temperatures (ca.  $400^{\circ}$ ) in the liquid phase over a static catalyst. From 100 gallons of lubricating oil stock, 105 gallons of product are obtained, the yields of final products being as follows :—

47.2	galls.	of light "Hydrolube."
20.3	"	" heavy "
28.3	"	" petrol and gas oil.
9.2	"	" wax.

Hydrogenated lubricating oils are characterised by high viscosity index and flash point and low Conradson carbon (tendency to form carbon deposit in internal combustion engines). The colour is greatly improved, and 80-90 per cent. of the sulphur in the feed stock is removed.<sup>44</sup>

In the refining of burning oils hydrogenation is similarly favoured and cracking suppressed, the process being operated at low temperatures in the vapour phase. From 100 gallons of crude low-grade kerosene distillate, 105 gallons of product are obtained, representing up to 85 gallons of high-grade kerosene together with petrol: 80-95 per cent. of the sulphur is removed.<sup>42</sup>

Heavy crude oils and refinery residues are treated in the liquid phase in a similar manner to that adopted for coal.<sup>42</sup> A volume yield of 101-104 per cent. is obtainable, 30-32 per cent. being petrol and the remainder a gas oil suitable for treatment in the vapour phase. Removal of sulphur to the extent of 65-85 per cent. is achieved.

Gas oils are converted into anti-knock petrol in the vapour phase at high temperatures ( $500^{\circ}$ - $540^{\circ}$ ). By re-cycling the unconverted gas oil, yields of 85-95 per cent. of gasoline can be obtained, the remainder representing conversion to gas. The throughput of raw material and the yield and anti-knock properties of the petrol depend on the type of catalyst employed: <sup>44</sup>

	Catalyst "A."	Catalyst "C."
Throughput, vols. total throughput per vol. catalyst space per hour	2.0	4.0
Vol. per cent. fresh feed	45	58
Vol. per cent. yield of petrol on fresh feed	86	90
Vol. petrol/vol. catalyst/hour	0.78	2.09
Octane number (measure of anti-knock value)	85	72

Catalyst "C" was a more active one than "A," and it will be seen that, although by virtue of its pronounced

hydrogenating activity the octane number is reduced, the yield of petrol per volume of catalyst per hour has been more than doubled.

Cracked, sulphur-containing naphthas are treated in the vapour phase at low temperatures and 100 per cent. volume yields of water-white, stable naphthas containing only traces of sulphur are obtained.<sup>42</sup>

In the production of "safety fuels" gas oils are treated in the vapour phase at high temperatures in order to obtain aromatic products. The latter are fractionated into two fractions, the low-boiling portion (up to  $150^{\circ}$ ) finding use as a high-grade aviation fuel, whilst the higher-boiling portion ( $150^{\circ}$ – $210^{\circ}$ ) forms the high flash-point safety fuel. A yield of about 30 per cent. of the former and 50–60 per cent. of the latter is obtained.<sup>43</sup> Special solvents are prepared in a similar manner. The hydrogenated product is distilled into a number of close fractions, *e.g.*,  $138^{\circ}$ – $191^{\circ}$ ,  $166^{\circ}$ – $204^{\circ}$ ,  $171^{\circ}$ – $221^{\circ}$ , to fulfil various uses in varnish and similar industries. They are characterised by a low sulphur content and solvent power equal to that of toluene and xylene.







## CHAPTER V

### THE INDUSTRIAL SYNTHESIS OF AMMONIA

THIS chapter is concerned mainly with the high-pressure catalytic processes which have been developed for the manufacture of ammonia from its elements. It has been desired, however, to survey the field of synthetic nitrogenous fertilisers and related compounds as fully as possible, and references to other materials than ammonia will be found in this and the following chapter. In particular, in this chapter, we have appended to the discussion of the ammonia synthesis some paragraphs dealing with the present-day production of cyanamide, urea and hydrocyanic acid.

#### The Economic Side of the Fixed Nitrogen Problem.

It is self-evident that the provision of adequate supplies of food for the increasing population of the world is as important a problem as any which confronts us, and in consequence the processes which form the subject of this and the succeeding chapter, owing to their far-reaching influence on the solution of the food supply problem, are more vital than any other methods of industrial catalysis.

With the exception of the *Leguminosæ*, growing vegetation is not able directly to convert the nitrogen of the air into combined nitrogen which can be utilised to elaborate the protein of plants. Nitrogen must be present in the soil in the "fixed" condition both as ammonium compounds and as nitrates, and the more intensively the soil is exploited the more necessary it becomes to replenish the stock of fixed nitrogen therein. To a certain extent this has long been done by growing legumes, by applying animal manures, and by ploughing-under green crops ("green manuring"), but these measures do not as a rule

suffice, and have been supplemented for nearly a century by the use of increasing amounts of artificial fertilisers, such as ammonium sulphate or nitrate of soda.

Until comparatively recent times, the sources of these materials were on the one hand by-product sulphate of ammonia, isolated from crude coal or coke-oven gas during purification, and on the other hand, natural sodium nitrate obtained from the deposits of this material in Chile.

The fundamental problem has been stated very clearly by Lt.-Col. G. P. Pollitt <sup>2</sup> as follows :—

“ There is a very direct connection between the increase in the world's population and the world's requirements of fixed nitrogen. It may be estimated that for at least 500,000 years a human being differing very little from his present form has inhabited the earth. In all that time up to 1800 A.D., the world's population has increased from its beginnings to a figure estimated at 800 millions. In the next 100 years from 1800 A.D. to 1900 A.D. it rose to 1,730 millions, that is, it more than doubled itself, and this rate of increase, or something approaching it, is continuing to-day. This rate obviously cannot be continued indefinitely under any circumstances ; it cannot go on at all unless the productivity of the soil keeps pace with it.”

The development of fresh tracts of virgin soil in all parts of the world will, in due course, reach its limit, and the only method then available will be to increase the output per unit of agricultural land, that is to say, to increase very largely the use of inorganic fertilisers, a most important constituent of which is fixed nitrogen. This was already apparent to Sir Wm. Crookes <sup>1</sup> many years ago when, in a famous address to the British Association in 1898, he emphasised the absolute necessity for preserving and adding to our nitrogen resources, and stated that the fixation of atmospheric nitrogen was one of the great discoveries awaiting the ingenuity of chemists.

This address certainly stimulated the search for commercial methods of producing ammonia or nitric acid from the atmosphere, although a certain amount

of laboratory investigation on the production of ammonia from nitrogen and hydrogen, either by the electric arc or by passage over metals such as titanium or iron, had already been carried out by Deville <sup>3</sup> (1865), Tessié du Motay <sup>4</sup> (1871), Tellier <sup>5</sup> (1881), Le Chatelier <sup>6</sup> (1901) and others.

About 1904 Birkeland and Eyde <sup>7</sup> worked out conditions under which, given sufficiently cheap electric power, air could be directly and economically converted into oxides of nitrogen by passage through an electric arc, a process which, though comparatively simple, involves a power consumption of about 65,000 kilowatt-hours per ton of nitrogen fixed. A little later, the fixation of nitrogen by combination with calcium carbide to give cyanamide was worked out technically by Frank <sup>37</sup> and Caro, <sup>38</sup> and this process (which is again referred to at the end of this chapter) has met with much success. It has now been established, however, that the cheapest and most economical process of nitrogen fixation is the combination of nitrogen and hydrogen at high pressure in presence of a suitable catalyst, forming ammonia, followed if desired by catalytic oxidation of the ammonia to oxides of nitrogen (nitric acid).

Before proceeding to describe the catalytic processes of ammonia synthesis it is not out of place to give a few statistics showing the development of the fixed nitrogen industry. The following table shows the world production of fixed nitrogen (expressed as metric tons of combined nitrogen) over a period of years up to the present time. Roughly speaking, we can take 1910 as a date immediately prior to the initiation of the synthetic ammonia industry.

It will be observed that the production of all forms of nitrogen, but particularly that of synthetic forms, increased enormously up to 1929, when it greatly exceeded world consumption. The serious falling-off in the succeeding years was due to the general depression in world trade, and particularly to the bad economic

*World Production and Consumption of Fixed Nitrogen  
(in metric tons of nitrogen).*

	1903.	1910.	1925.	1929.	1931.	1933.	1935.	1936.
<b>Production</b>								
Ammonium sulphate								
By-product	—	206,000	343,500	376,000	359,594	257,719	315,905	365,000
Synthetic	—	—	401,600	485,000	349,087	559,984	519,829	630,000*
Cyanamide	—	—	166,300	210,000	200,932	168,495	238,448	270,000*
Nitrate of lime	—	—	37,500	136,000	110,585	118,241	153,113	150,000
Other synthetic forms	—	—	—	365,000	393,150	462,060	591,242	720,000*
Other by-product forms	—	—	15,300	51,000	30,940	39,560	44,429	45,000
Chile nitrate	—	382,000	391,200	490,000	250,000	70,800	178,400	192,000
<b>Total production</b>	340,000	588,000	1,355,300	2,113,000	1,694,288	1,676,859	2,041,366	2,378,000*
<b>Total consumption</b>	—	—	—	1,872,080	1,621,305	1,746,947	2,030,161	2,400,000*

\* These figures are the highest on record in the respective categories.

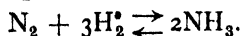
position of agriculture. In recent years production has increased again, but has been controlled to conform with demand. It is striking to note that in 1933 the amount of synthetic ammonium sulphate produced was alone almost equal in amount to the total production of fixed nitrogen in 1910.

Synthetic ammonia plants have been erected in most industrial countries, expansion of the industry in Russia, Germany and Japan being particularly marked in recent years. During 1935, the existing plants operated at only 43 per cent. of their full capacity, the world production capacity for synthetic nitrogen (including cyanamide) being then estimated at 3,490,000 tons per annum ; in 1936, the " synthetic nitrogen " factories operated at 48 per cent. capacity, the total capacity being 3,700,000 tons per annum.

The widespread development of the synthetic nitrogen industry has tended to make the recovery of by-product sulphate of ammonia by gas manufacturers uneconomic. The working-up of ammonia liquors, however, is compulsory by law, and the larger concerns are now stated to make a " modest profit " by this undertaking.

#### Theoretical Aspects of the Synthetic Ammonia Process.

The synthetic ammonia process depends ultimately, on the equilibrium point attainable in the change



At the time of the earlier attempts to produce ammonia in the presence of metals referred to above, the equilibrium data could at best be determined empirically ; with the help of Nernst's heat theorem it has become possible, given a number of experimental determinations at various temperatures and pressures, to calculate the composition of an equilibrium mixture over an extended range of temperatures and pressures. This was first carried out in the case of the ammonia equilibrium by Haber <sup>8</sup> and Le Rossignol <sup>9</sup> and co-

workers,<sup>11</sup> followed by Nernst and Jost,<sup>12</sup> experimental values being obtained over a range up to 70 atmospheres. More recent determinations of the ammonia equilibrium were made by Larson and Dodge<sup>13</sup> in 1923 and 1924, covering a range of pressures over 10–1,000 atmospheres and a wide range of temperatures. The Haber and Nernst figures for the lower range of pressures were satisfactorily confirmed. The nature of the technical problem will be gauged when it is said that at 100 atmospheres pressure the percentage of ammonia in the equilibrium mixture ranges from 80 at a temperature of 200°, through 25 at a temperature of 400°, 10.4 at 500°, 4.5 at 600°, 1.1 at 800° to 0.44 at 1,000°, whereas the rate of establishment of equilibrium falls to a very small value as the temperature decreases. The following table gives the percentage of ammonia at equilibrium over the temperature range 350°–500° for pressures of 1–1,000 atmospheres.

*Per Cent. NH<sub>3</sub> in Equilibrium Mixture.*

Pressure (atm.).	1	10	30	50	100	200	300	400	1,000
Temp.									
350° .	—	7.37	17.80	25.11	—	—	—	—	—
375° .	—	5.25	13.35	19.44	30.95	—	—	—	—
400° .	0.44	3.85	10.09	15.11	24.91	36.3	—	—	—
425° .	—	2.80	7.59	11.71	20.23	—	35.5	53.6	69.4
450° .	—	2.04	5.80	9.17	16.36	—	—	—	—
475° .	—	1.61	4.53	7.13	12.98	—	31.0	47.5	63.5
500° .	0.13	1.20	3.48	5.58	10.40	17.6	26.2	42.1	—

Prior to the work of Haber and Le Rossignol no means were known of attaining the equilibrium in a technically useful time at temperatures below about 800°, at which it will be seen the conversion to ammonia is extremely small. They proceeded to search for and to discover materials which would promote the more rapid attainment of equilibrium at considerably lower temperatures, that is, as low as 400°–500°. Thereby



they rendered a service greater even than their equilibria data, and paved the way for modern practice.

It is, perhaps, unnecessary here to go more deeply into the purely theoretical side of the ammonia synthesis, except to point out that under working conditions a higher output of ammonia can usually be obtained by not allowing the gases to remain in contact with the catalyst sufficiently long for complete attainment of equilibrium. In other words, in accordance with the law of mass action the later stages of approach to equilibrium proceed much more slowly than the initial part of the conversion of the nitrogen-hydrogen mixture to ammonia, so that, if the rate of passage of the gas mixture is increased, for example, ten times, this may very well result in, say, half the amount of ammonia being produced at any given passage of the gas at the higher rate of flow compared with that at the lower rate; but it is obvious that even so, in a given time five times as much ammonia would actually be produced at the higher rate of flow than at the lower. Haber and Greenwood<sup>10</sup> give data for ammonia output in presence of a uranium carbide catalyst at  $515^{\circ}$  and 114 atmospheres pressure, which illustrate this point.

*Space-time-yield of Ammonia at  $515^{\circ}$  and 114 Atmospheres (Haber and Greenwood).*

Litres gas per litre catalyst space per hour	5,800	31,650	82,600	194,000
Percentage of ammonia (volume) produced	7.63	6.42	4.78	4.18
Kg. ammonia per litre catalyst space per hour.	0.318*	1.46	2.84	5.83

The general conclusions to be drawn from the theoretical work which has been carried out on this problem, therefore, assume the following form:—

(1) The conversion of a nitrogen-hydrogen mixture to ammonia becomes relatively high at pressures of the order of 1,000 atmospheres, and is sufficiently high for

technical success from about 100 atmospheres pressure onwards, at all events at temperatures from  $600^{\circ}$  downwards.

(2) Formation of ammonia is favoured by low temperature, but in the absence of catalysts the attainment of equilibrium is exceedingly slow even at high temperatures ( $800^{\circ}$ – $1,000^{\circ}$ ), at which, in any case, the percentage of ammonia at equilibrium is too small to be of practical interest.

(3) The attainment of equilibrium can be accelerated to a marked degree by the employment of appropriate catalysts which, as at present understood, are active from about  $400^{\circ}$  upwards.

These principles have been applied technically in various ways, and a description of the various synthetic ammonia processes now in operation consists essentially of an account of these variations.

#### Catalysts Employed in the Synthesis of Ammonia.

Haber and his co-workers studied the action of a variety of metallic catalysts and apparently favoured osmium and uranium as the most active catalysts; iron, nickel, manganese and other metals of the seventh and eighth groups of the Periodic System were also found suitable. In actual practice the rarer metals mentioned have been found unsuitable either on the score of cost or because of their susceptibility to catalyst poisons, and the basis of most of the catalysts in use at the present day is probably pure iron. At the same time it has become evident that the addition of small amounts of alkaline materials greatly stimulates the action of the iron catalyst, and many patents have been taken out for the production of different types of iron-alkali catalysts.<sup>14</sup>

Thus it may be mentioned that whilst Casale<sup>15</sup> advocates that the iron should be prepared by fusion of pure iron turnings with an alkaline-earth oxide (lime) in a current of oxygen, followed by subsequent reduction of the iron oxide formed, Collett and

Synthetic Ammonia and Nitrates, Ltd.<sup>16</sup> recommend the fusion of 160 parts of pure ferric oxide with 56 parts of lime at  $1,200^{\circ}$ , followed by reduction of the calcium ferrite thus formed. Lush<sup>17</sup> employs anodic oxidation of pure iron turnings in a bath of potassium carbonate (on similar lines to his fat-hydrogenation catalyst, *cf.* this Section, Chapter XI., p. 283), followed by reduction of the catalyst without washing away the adherent alkaline carbonate. The Du Pont Ammonia Corporation<sup>18</sup> prepare a suitable catalyst by fusing a mixture of potassium carbonate, magnesium oxide, silica and ferroso-ferric oxide, crushing the melt to uniform granules followed by reduction at  $400^{\circ}$ – $800^{\circ}$  in hydrogen or a 3 : 1 hydrogen-nitrogen mixture. Titanomagnetite fused with potassium aluminate has been claimed as an active catalyst.<sup>19</sup> It has been stated<sup>20</sup> that the catalyst employed by the I.G. in their Leuna plant consists of "specially pure iron activated by small proportions of alkali and alumina."

The function of the catalyst in the ammonia synthesis has been studied from the point of view of adsorption,<sup>21</sup> and it is clear that, as usual, a material which acts as a catalyst for the production of ammonia must possess a capacity for selective adsorption of both hydrogen and nitrogen. The amount of adsorption has been shown to be considerably increased in presence of the alkali, although the precise function of this or any other catalyst promoter is still by no means clearly understood. Recent work has suggested that the synthesis takes place through the intermediate formation of a film of metallic nitride, in the following manner :—



Thus the velocity of decomposition of ammonia on iron catalysts has been shown<sup>22</sup> to depend on the rate of formation of the nitride. Similarly, it was concluded from studies with tungsten catalysts that hydrogenation occurred in a nitride film. The adsorption of hydrogen

and ammonia on tungsten took place in a normal manner, but adsorption of nitrogen was found to be irreversible and to increase with increase in temperature.<sup>23</sup>

#### Technical Sources of Hydrogen and Nitrogen for the Ammonia Synthesis.

In commencing to describe the actual technical procedure involved it is important to consider first of all the relative merits of different sources of hydrogen and nitrogen. In discussing the methods of hydrogen manufacture in Chapter II of this Section reference was made to the variations in procedure necessary to produce a 3 : 1 hydrogen-nitrogen mixture for ammonia synthesis. Thus, in the water-gas catalytic process, a mixture of water-gas and producer-gas, or of both gases with air, is employed in suitable proportions to lead, finally, to a mixture of hydrogen and nitrogen in the correct ratio. In Germany, the gas to be submitted to the catalytic process is prepared by burning lignite at 1,000° in a Winkler generator using a 50-50 mixture of oxygen and nitrogen together with steam in a continuous process. Gaseous hydrocarbons in the form of natural gas or coke-oven gas are partially combusted with air or treated by the methane-steam process combined with partial combustion and the resulting carbon monoxide-hydrogen-nitrogen mixture further treated by the catalytic water-gas process. Finally, there is the electrolytic production of hydrogen and the production of the necessary nitrogen from liquid air or other separate source.

It has been stated by Polkitt<sup>24</sup> that, having obtained the nitrogen-hydrogen mixture, there is no significant difference between the costs of the actual synthesis of ammonia by the various processes employed: the cost of the total process in each case is determined by the source of hydrogen: Pollitt gives the costs of producing one metric ton of ammonia using different sources of hydrogen as follows :—

Source of Hydrogen.	Cost of Ammonia (£ per m.t.)
Electrolysis	
H.T.A.C. current at 0.05d./kw.h. .	7.0
0.10 „ .	9.3
0.15 „ .	11.7
Coke-oven gas . . . . .	9.0
Water-gas . . . . .	7.2

The figure for coke-oven gas has been criticised by Parrish,<sup>25</sup> and in view of the widespread use, more particularly on the Continent, of this gas as the raw material, the figure given is probably high, relative to that for water-gas. A nitrogen-hydrogen mixture derived from water-gas or coke-oven gas must be submitted to a rigorous and expensive purification process to remove carbon monoxide and hydrogen sulphide, but although electrolysis yields very pure hydrogen, it is clear that the cost of electricity must be very low before this source of hydrogen becomes economic. In Norway the "arc process" of nitrogen fixation has almost entirely disappeared, and cheap electric power has been liberated for the electrolytic production of hydrogen for the ammonia synthesis. Electrolytic hydrogen is also employed in Switzerland and Northern Italy, and in one of the fourteen ammonia plants in France. The remaining French plants employ coke-oven gas as the source of the gas mixture, as is also the case in Germany, except, as at Leuna, where the proximity of large lignite deposits provide an alternative source. In England, coke water-gas still forms the main source of the gas mixture.

In one of the processes about to be described, in which electrolytic hydrogen is mainly employed,<sup>26</sup> the necessary nitrogen is obtained by oxidation of a portion of the ammonia output with air as described in the next chapter, p. 182, forming nitric acid; the residual nitrogen from the air employed in oxidising the ammonia, which amounts to about 5 volumes of

nitrogen for every volume of ammonia oxidised, provides ample supplies for the synthesis of further quantities of ammonia. Another procedure<sup>27</sup> is to burn a mixture of air and hydrogen under the boilers used for raising steam, condensing the water for electrolysis and using the residual nitrogen for admixture with hydrogen.

#### Technical Processes in Use for Combining Nitrogen and Hydrogen.

There are five main types of process, namely, the Haber-Bosch and the Fauser, Casale, Claude and Mont-Cenis (Uhde) processes. These will be discussed in this order, and it will be gathered that the chief differences between them are in the pressures employed, the source of the gas mixture, and the means adopted for the removal of the ammonia produced.

(1) *The Haber-Bosch Process*.<sup>28</sup>—This process was developed on the large scale by the Badische Anilin und Soda Fabrik, now included in the I.G. Farbenindustrie A.-G. The gas mixture derived from coke or lignite water-gas consists approximately of 25 per cent. nitrogen and 75 per cent. hydrogen, and is compressed in five stages to 220 atmospheres, namely, from 1 to 3 to 9 to 30 to 90 and finally to 220 atmospheres. Carbon dioxide is removed at the 30 atmospheres stage by scrubbing with water; the gas is then compressed up to 220 atmospheres and the carbon monoxide removed, as described in this Section, Chapter II, p. 87. The purified nitrogen-hydrogen mixture is passed through a series of small catalyst chambers to remove catalyst poisons, and is then circulated rapidly through the main ammonia converters, a yield of about 8 per cent. of ammonia being obtained at each passage.

The converters consist of cylinders 20 ft. high and 2 ft. in diameter, constructed of special steel enclosing an internal vessel of ordinary mild steel  $\frac{3}{8}$ – $\frac{1}{2}$  inch thick. In course of time the internal lining becomes

decarbonised by the hydrogen and permeable to the latter gas, and in order to prevent accumulation of gas between the internal and the external cylinders, the latter are drilled throughout their length with  $\frac{3}{16}$  inch holes. Each cylinder is placed in a separate compartment on one side of a heavy concrete wall, on the other side of which are ranged all the gas and temperature controls. The flow of gas is adjusted continuously and mainly automatically. The temperature control is also largely automatic, the process being carried on by the slight heat developed in the reaction. The interior of the converters is maintained at  $550^{\circ}$ – $600^{\circ}$ , and the exterior of the shell at about  $300^{\circ}$ – $400^{\circ}$ . The exit gases, still at the pressure of 200 atmospheres, are scrubbed through water and the wash water is released through a thick glass tube supported in a slotted steel pipe; the ammonia solution is converted into sulphate by adding carbon dioxide and stirring the ammonium carbonate liquor with a suspension of gypsum or anhydrite, as described below. Sufficient hydrogen and nitrogen are dissolved in the water at the high pressure employed to make it worth while to scrub the gases, released when the water is brought to atmospheric pressure, through a water tower which removes ammonia from the recovered nitrogen and hydrogen, the latter being re-circulated over the catalyst.

As the nitrogen and hydrogen are removed from the gas mixture the amount of inert hydrocarbons, etc. (originally small) becomes sufficiently great to retard the process and from time to time these are drawn off. The whole process is thus largely controlled automatically and requires a minimum of manual supervision.

The first of the Badische plants was erected at Oppau in 1911–1912 and came into operation shortly before the outbreak of war, 1914, with an output of 130,000 tons of fixed nitrogen per year; in 1917 an additional plant was erected at Merseburg with an

ultimate output of 350,000 tons of fixed nitrogen per year. More recently a large plant has been erected at Leuna, where the process is operated very conveniently in conjunction with other high-pressure catalytic processes, namely, the methanol synthesis and the hydrogenation-cracking of lignite.

The British plant at Billingham-on-Tees, operated originally by Synthetic Ammonia and Nitrates Ltd., now a subsidiary of Imperial Chemical Industries Ltd., has been developed on the lines of the original Haber process, which has been modified and adapted to the local conditions. It has been stated that the company's experts are satisfied that the alternative methods described below do not offer any advantages under English conditions over the general scheme of the Haber process. The nitrogen-hydrogen mixture is obtained from coke water-gas and producer-gas as in certain of the I.G. plants; the working of the ammonia converters is on somewhat similar lines, and at present the bulk of the ammonia produced is converted into sulphate by interaction of ammonium carbonate and calcium sulphate, the latter being obtained from a large deposit of anhydrite situated near the site of the works on Teeside. Although the general principles of the Haber-Bosch method have been employed at Billingham as the foundation of the process, it is understood that many alterations in detail have been made, especially as regards plant construction; the efficiency of the Billingham plant marks a considerable improvement over that of the original German plants.

(2) *The Fauser and Casale Processes.*—These modifications of the original Haber-Bosch process may be considered together because their main difference is the use of somewhat higher pressures in the ammonia converters, namely, from 300–500 atmospheres. Various other differences in operation will be observed, but these usually arise from economic factors which, for example, render modifications in the production of the



original nitrogen-hydrogen mixture desirable. These processes are in operation in Italy, Switzerland and France, and to a less extent in Germany and other countries. In 1929, rather less than half the total French synthetic ammonia output was produced by the Casale process. In 1930 the Fauser process appeared to be gaining popularity, the total capacity of Fauser plants at that date being about 300,000 tons of ammonia per annum.<sup>29</sup>

The Fauser<sup>26</sup> process is concerned with the conversion of electrolytic hydrogen into ammonia, so that simultaneous production of nitrogen from producer-gas becomes impracticable. A small plant for the catalytic oxidation of ammonia to nitric acid is therefore added to the main ammonia plant, and in this a certain proportion of the ammonia output is mixed with air and converted to nitric acid. The residual gases from the nitric acid scrubbers consist of nitrogen with small amounts of unused oxygen; these are mixed with hydrogen and passed over heated platinised-asbestos, when all the oxygen is converted into water and the purified nitrogen is ready for mixing with electrolytic hydrogen and passage through the ammonia converters. As already stated, one volume of ammonia furnishes in this way five volumes of nitrogen, which, in turn, are ultimately capable of producing 10 volumes of ammonia, so that theoretically it is only necessary to oxidise 10 per cent. of the ammonia output in order to obtain sufficient nitrogen from the air for production of the total ammonia output required. A recent patent,<sup>30</sup> which claims the preparation of a gas mixture suitable for ammonia synthesis by the gasification of carbon with steam and air under pressure, suggests that the use of electrolytic hydrogen in the Fauser process may be ultimately abandoned. The ammonia converters are somewhat similar to those used at 200 atmospheres, allowance, of course, being made for resistance to the higher pressures employed, and for the fact that less

space is required for the production of a given amount of ammonia in a given time at the higher pressures. In the Fauser process the exit gases are submitted to refrigeration and a considerable proportion of the ammonia is removed in the liquid state, that remaining being scrubbed out with water as in the other systems.

The Casale process<sup>27</sup> is also designed mainly for the use of electrolytic hydrogen. Nitrogen is obtained by burning the oxygen of the air with hydrogen, and the water formed is condensed and used in electrolysis, which requires particularly pure water. The chief characteristic of the process, however, is said to be the introduction and maintenance of a certain percentage of ammonia in the nitrogen-hydrogen mixture. The ammonia prevents overheating of the catalyst as equilibrium is established at the catalyst surface, and this tends to reduce the working temperature, and to maintain a higher conversion than if the temperature were allowed to rise locally; it also increases the specific heat of the gas mixture, thus contributing to efficient heat interchange. The Casale method of preparing the catalyst has already been mentioned above; the process is designed to work at 300–500 atmospheres and about 600°, and is otherwise very similar in operation to the Fauser process.

- (3) *The Claude Process*.<sup>31</sup> This process works at 900–1,000 atmospheres, that is, at much higher pressures than any of the preceding methods; the advantages claimed are speed of conversion in the actual combination, small size of plant required for a given output, rapidity of starting up the plant, and, finally, it is stated that the Claude plant is the only one which is suitable for the production of comparatively small quantities of ammonia—for example, for small units giving about 5 tons per day of fixed nitrogen. The principle of the process is exactly similar to that of the Haber-Bosch method except for the difference in pressure. Either water-gas or electrolytic hydrogen may be employed and Claude has also suggested

processes for the recovery of hydrogen from coke-oven gas, by liquefaction,<sup>32</sup> for use in the ammonia synthesis.

The amount of ammonia formed per hour per litre of catalyst space is stated to be 5,600–6,700 gm. by the Claude system as against 350–400 gm. by the Haber process, in consequence of the much higher percentage of ammonia at equilibrium at 1,000 atmospheres. Similarly, the heat evolved by the reaction is also much greater per unit of converter space, and consequently it is possible to use quite small vessels without encountering difficulties in radiation losses. The Claude catalyst tubes are of high tensile alloy, cast solid and bored out and the customary peroxidised-iron catalyst is used. The gas mixture is passed through four sets of catalyst tubes, traversing the first two in parallel, the gas streams being then united and passed in series through the second pair of tubes; ammonia is removed from the reacting gases by cooling between each passage over the catalyst. Starting all cold, a Claude plant will begin to produce ammonia in between 4 and 5 hours, whereas the Haber system requires three days.<sup>33</sup>

The apparent difficulty of compressing the gases to and circulating them at such extremely high pressures, owing to leaks at joints and valves, is more than compensated for by the fact that, owing to the high pressure, the pipe connections, etc., need only be of relatively small diameter, and consequently it is much more easy to render joints and valves effectively gas-tight. Finally, 97–98 per cent. of the ammonia produced can be removed in the liquid state by simple water-cooling of the exit gases from the converters, and it only remains to absorb the residual 2–3 per cent. of unliquefied ammonia in sulphuric acid.

The Wintershall Co. of Germany erected a Claude plant in 1928, employing coke-oven gas as raw material, and it has been stated that in 1929 more than half the annual production of ammonia in France was by the Claude process. The Du Pont Ammonia Corpora-

tion of America employ pressures of the same order as those of the Claude process (1,000 atmospheres), and the manufacture of ammonia is combined with that of methyl alcohol. The methyl alcohol converters are utilised to remove the carbon monoxide from the crude water-gas, which then passes to the ammonia converters. The ammonia is obtained and stored in liquid form.<sup>34</sup>

(4) *The Mont-Cenis (Uhde) Process.*<sup>35</sup>—The process based on the patents of G. F. Uhde appears to differ from the others in the use of relatively low temperatures and pressures. Few details have been made public concerning the process, but the patents indicate the use of a temperature in the region of 400° and a pressure of 100 atmospheres or less.

These mild conditions are said to be made possible by the use of a very active catalyst consisting of complex ferrocyanides such as a potassium-aluminium-ferrocyanide most suitably prepared in non-aqueous solution, *e.g.*, in acetic anhydride as solvent. The gases are purified by passage through molten alkali metal amides at 200°–300° and under pressure. To avoid overheating of the catalyst, the reaction chamber is fitted with double-walled pipes, the gases passing through the inner pipe, the outer annulus, and the catalyst bed in successively reversed directions. The ammonia is separated from the reaction gases in the liquid state by refrigeration produced by the evaporation of previously obtained liquid ammonia.

The process was operated on a large scale at Solingen by the Gewerkschaft der Steinkohlenzeche Mont-Cenis in 1927, and has since become established in Holland, Germany, France and America.

#### Combination of Ammonia as Solid Salts for Marketing.

As already indicated, the bulk of the synthetic ammonia produced is converted into sulphate. At first this was effected similarly to the production of by-product sulphate of ammonia, namely, by direct

neutralisation of the ammonia with dilute sulphuric acid followed by crystallisation. It was soon realised, however, that the use of free sulphuric acid was an extravagance, for by combining the ammonia produced with carbon dioxide (usually available as a by-product in the manufacture of the hydrogen required) it is possible to produce ammonium sulphate by double decomposition with a suspension of calcium sulphate :—



As calcium sulphate occurs fairly abundantly in the form of gypsum and anhydrite, this procedure has become general both in Germany and in England—the site for the main British works having, in fact, been chosen partly in consequence of nearness to a large deposit of this mineral.

Sulphate of ammonia, however, is by no means the only form of fixed nitrogen which is desired by the agriculturalist, and other forms of so-called compound fertilisers have also to be taken into account. An important matter is the provision of nitrate fertilisers in substitution for sodium nitrate, and for this purpose ammonia is oxidised to nitric acid, the latter being further combined with ammonia to form ammonium nitrate ; a mixture of the latter with chalk (by-product calcium carbonate), termed nitro-chalk, is another of the modern forms of fertiliser. The Germans, in order to overcome the 'deliquescent' properties of ammonium nitrate, manufacture a double nitrate and sulphate of ammonia, but the stability of this material, especially when stored in bulk, is uncertain, and had some connection with the disastrous explosion at Oppau in September, 1921. Again, phosphates are necessary ingredients of many agricultural fertilisers, and a certain amount of ammonia is converted into ammonium phosphate by double decomposition of the carbonate with calcium phosphate, or by direct combination with phosphoric acid produced from arc-

process phosphorus. To a smaller extent, ammonium carbonate itself is required for certain purposes.

The plant necessary for converting ammonia into any of these solid salts is more or less standardised in type, and consists of agitators for effecting the double decomposition, followed by settling or filtration and concentration of the clear liquor to crystallisation in double- or triple-effect vacuum evaporators.

### The Production of Cyanamide.

After calcium carbide became a commercial product, about 1895, attempts were made to utilise it as a basis for fixing atmospheric nitrogen. Between 1904 and 1908 large-scale plants were put into operation by Frank <sup>37</sup> and Caro, <sup>38</sup> in which the carbide was heated to a temperature of  $800^{\circ}$ – $1,000^{\circ}$  and a current of nitrogen passed over it. It had already been shown by Moissan <sup>36</sup> that pure calcium carbide did not fix nitrogen below  $1,200^{\circ}$ , but it was found that the commercial carbides absorbed nitrogen at somewhat lower temperatures, and that this was due to a kind of catalytic action exerted by small amounts of metallic chlorides which were present. In the actual technical process, therefore, a quantity of calcium chloride (for example, up to 10 per cent. of the carbide in process) was added to the reaction mass, and under these conditions absorption of the nitrogen to the extent of 20 per cent. or more of the weight of carbide proceeds at about  $800^{\circ}$ . The reaction involved is as follows:—



At higher temperatures, for example  $1,200^{\circ}$  and above, direct addition of nitrogen with formation of calcium cyanide,  $\text{Ca}(\text{CN})_2$ , also takes place in appreciable amount, and the function of the metallic chloride catalyst employed in the Frank-Caro process is thus not only to lower the temperature of reaction, but simultaneously to avoid producing the undesired cyanide.

The present production (1936) of cyanamide is in the neighbourhood of 800,000 tons, corresponding to over 200,000 tons of fixed nitrogen per annum. In one form of the process, the crushed carbide is heated in an electric furnace consisting of carbon rods passing down the centre of a number of iron drums lined with refractory bricks, whilst a current of nitrogen is passed through the series. The reaction is exothermic and proceeds after initiation by its own heat; the temperature is not allowed to exceed  $1,000^{\circ}$ – $1,100^{\circ}$ . About 20 per cent. of nitrogen is absorbed in the course of some twenty-eight hours, after which the drums are cooled and the product removed, pulverised, washed with water, and used mainly as a fertiliser under the name Nitrolim. Alternative methods are slowly to pass a series of trucks containing carbide through gas-heated airtight tunnel-ovens in which an atmosphere of nitrogen is maintained, or to pass a mixture of powdered carbide with calcium chloride or fluoride down a vertical furnace, fitted with alternating shelves which are heated electrically.

Whilst the main use of cyanamide is directly as a fertiliser, it serves other purposes, one of which is its conversion into urea.

#### The Production of Urea.

Many people hold the opinion that nitrogen can be more efficiently supplied to the soil in the form of urea,  $\text{CO}(\text{NH}_2)_2$ , than as ammonium salts. It is considered that nitrogen can be assimilated by the plant most readily when it is combined simply with carbonic acid, but ammonium carbonate and carbamate are dissociated too readily into ammonia and carbon dioxide to permit them to be efficient conveyors of ammonia to the soil.

Urea, first synthesised by Wöhler more than 100 years ago, has only lately been prepared on an industrial scale; over 9,000 tons of it were made in Germany in 1926–1927. Theoretically, urea should be an ideal

source of nitrogenous plant-food ; practically, it may be said not to have come quite up to expectations. It has given excellent results on grassland, in garden and glasshouse, and also on rubber plantations in Southern India, where it has proved very successful as an antidote to the disease of rubber trees known as "Secondary Leaf-Fall." It is, moreover, very concentrated, containing 46 per cent. of nitrogen, and is thus economical in use and transport. Unfortunately, however, urea, being readily soluble in water, is leached out of arable soils almost as readily as sodium nitrate ; it is also hygroscopic and therefore difficult to store in humid climates. Further, experience has shown that it does not mix well with superphosphate or low-grade potash salts.

Urea is obtained technically either from calcium cyanamide or by direct union of ammonia and carbon dioxide.

*Urea from Cyanamide.*—Careful treatment of cyanamide in concentrated aqueous solution with small amounts of sulphuric acid at about  $70^{\circ}$ – $80^{\circ}$  leads to the formation of urea. The more intensive action of water or steam converts the material entirely into ammonia and calcium carbonate, and the process is not one which lends itself too readily to high yields of urea. Consequently, although a certain amount of urea is technically produced from cyanamide as a fine chemical, the cost of production by this method may not permit urea to be marketed at the low price demanded by the fertiliser industry.

*Urea from Ammonia and Carbon Dioxide.*—Within the last few years the possibility has been carefully investigated of employing the following reactions on a technical scale, and it would appear that successful processes for the production of urea from ammonia and carbon dioxide are now in being :—

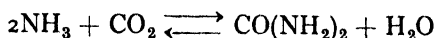


Theoretical data on the equilibria involved in these



changes have been published by Matignon and Fréjacques<sup>39</sup> (1920-1922), and several descriptions have been given in the patent literature and elsewhere of means by which this reaction can be carried out on a large scale.

Thus the Badische Anilin und Soda Fabrik<sup>40</sup> describes a process in which two volumes of ammonia and one volume of carbon dioxide are heated for two hours under a pressure of 50-100 atmospheres and at a temperature of 135°-150°. Under these conditions a state of equilibrium is reached in the interaction



in which about 40 per cent. of urea is present. The liquid product is either slowly released into a distilling column, when unchanged ammonium carbamate is decomposed into ammonia and carbon dioxide; or the latter may be removed by cooling the charge in the autoclave to 60°-100° and reducing the pressure, when the same result is obtained. The recovered gases are compressed again and used in the production of further quantities of urea. The concentrated solution of urea leaving the still is further evaporated in vacuum concentrators and, according to another Badische patent, is obtained as a highly concentrated solution, which may be distributed into a chamber in the form of a moderately coarse spray; the drops then solidify in sandy grains which are suitable for use as a fertiliser.

A Norwegian process<sup>41</sup> for producing urea consists in passing carbon dioxide at 130°-140° over ammonia compounds mixed with salts such as ammonium chloride or calcium chloride, when conversion to urea takes place, and the cooled product, after pulverisation, may be used directly as a fertiliser.

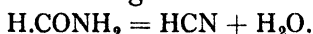
It will be noticed that the condensation of ammonia and carbon dioxide to urea, at all events by the Badische process, does not involve the employment of catalysts, but it is appropriate to refer to the method here since

it forms one of the outlets for synthetic ammonia produced by the catalytic process, whilst, in practice, the carbon dioxide used would generally be obtained from the operation of the catalytic water-gas hydrogen process carried on in conjunction with ammonia synthesis.

#### The Catalytic Production of Hydrocyanic Acid.

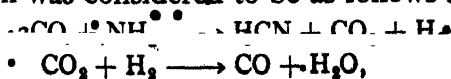
A number of processes have been developed in recent years for the production of hydrocyanic acid, which finds use in organic chemical syntheses and as a fumigant.

One process employs the dehydration of formamide according to the following reaction :—

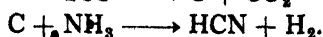
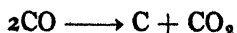


Thus the I.G. Farbenind. A.-G. claim <sup>42</sup> that formamide vapour is completely converted into hydrocyanic acid and water by treatment at 400°–450° under reduced pressure in the presence of dehydrating catalysts such as natural or artificial zeolites, calcium chloride, or carbonates of the alkali metals. A similar process employing as catalyst alumina, zirconia or thoria has been patented by I.C.I. Ltd. <sup>43</sup> In place of the formamide a mixture of ammonia and carbon monoxide may be employed. In a process developed by the I.G. <sup>44</sup> a mixture of carbon monoxide with 10–12 per cent. of ammonia is passed over a catalyst comprising carbides of iron, nickel or cobalt at 450°. The hydrocyanic acid is recovered either by condensation or by absorption in caustic alkali.

A study of this type of process has been made by Bredig and co-workers, <sup>45</sup> who found that the best yields of hydrogen cyanide were obtained at temperatures in the range 500°–700°, in the presence of alumina or ceria deposited on alumina. From a study of the kinetics of the process the most probable mechanism was considered to be as follows :—



together with side reactions :—



More recently, Fuchs and Verbeek <sup>46</sup> have claimed high yields of hydrogen cyanide by passing a mixture of ammonia and carbon monoxide in the ratio 1 : 9.4 at 570° over a catalyst prepared by adding concentrated ammonia to a solution of aluminium nitrate and treating the dried precipitate with a solution of a zirconium salt.

Other processes employ a mixture of ammonia and hydrocarbon gases or vapours. Bredig <sup>47</sup> found that 70 per cent. yields of hydrogen cyanide were obtained by treating a mixture of equal volumes of ammonia and ethylene at 700° in the presence of a pure alumina, or mixed quartz and alumina, catalyst. Hydrocyanic acid for the fumigation of ships and empty warehouses is produced by the Koppers Co.<sup>48</sup> of America in the form of a 96–98 per cent. aqueous solution. Ammonia is passed through benzene at 28° in 6 : 1 ratio or through toluene at 50°–55° to give a 7 : 1 ammonia : hydrocarbon ratio and the mixture is passed over kieselguhr impregnated with alumina at 1,100°–1,150°. Hydrogen is produced together with hydrogen cyanide. A new process, also stated to be employed technically, has been developed by Andrussov.<sup>49</sup> A mixture of ammonia, air and methane in the volumetric ratio 2 : 14.4 : 2 is passed through platinum gauze at 1,000°. The methane is said to combine with “nitroxyl”—a primary product of the oxidation of ammonia—to produce hydrogen cyanide. Some 60 per cent. of the ammonia is recovered as hydrocyanic acid, 10 per cent. is lost as nitrogen and the remainder passes through unchanged.

## References to Section II., Chapter V

### GENERAL

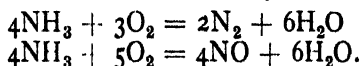
Sir W. CROOKES. *Brit. Assoc. Reports*, 1898 ; J. R. PARTINGTON and L. H. PARKER, “The Nitrogen Industry” (1922).



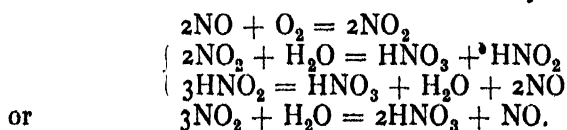
## CHAPTER VI

### THE INDUSTRIAL CONVERSION OF AMMONIA INTO NITRIC ACID

THE catalytic production of nitric acid has been developed concurrently with the commercial synthesis of ammonia. Just as synthetic ammonia has relegated by-product sulphate and other forms of ammonia to a position of relatively minor importance, so also the production of nitric acid from Chile nitrate and sulphuric acid has been almost completely superseded by the catalytic oxidation of ammonia to nitric acid. It has been known for many years that ammonia can be directly oxidised in either of the following ways :—



Obviously if the oxidation can be controlled so that only the second of these processes comes into operation, nitric acid can be produced by the well-known further oxidation of nitric oxide, namely :—



The possibility of converting ammonia into nitric acid by passage of a mixture of the gas with air over heated spongy platinum was observed by Kuhlmann<sup>4</sup> in 1839, but no attempt was made to develop the process industrially until early in the present century, when Ostwald,<sup>5</sup> Frank and Caro,<sup>6</sup> and others worked out the technical conditions for an efficient process.

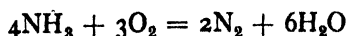
The Badische Company became interested in the matter from about 1910 onwards, when they were concerned with the development of synthetic ammonia in Germany, whilst contributions were also made by

F. Bayer & Co., and other German firms, all of whom are now constituents of the Interessengemeinschaft. In England the problem was systematically studied during the war period of 1914-1918 by the Ministry of Munitions, and a number of plants came into operation; subsequently the process was taken up by independent firms, notably the United Alkali Company and Synthetic Ammonia and Nitrates, Ltd., both of whom now form groups within Imperial Chemical Industries. Considerable attention has also been paid in the United States of America to the catalytic oxidation of ammonia, both by the United States Government chemists and by several of the large industrial corporations.

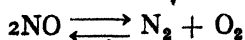
Two distinct forms of catalyst have been proposed for the process, namely (i) metallic gauze made of platinum or a similar metal, or (ii) mixtures of metallic oxides, generally comprising a large proportion of ferric oxide with a smaller amount of certain other oxides such as, for example, that of bismuth. The latter type of catalyst has attracted attention, of course, in view of the somewhat heavy primary cost of installing platinum catalysts.

#### Theoretical Aspects of the Catalytic Oxidation of Ammonia to Nitric Acid.

Thermodynamical considerations and practical experience agree in showing that at practically any temperature the oxidation of ammonia is complete, so that quantitative yields should always be obtained, unless side reactions enter into question. In point of fact, the reaction

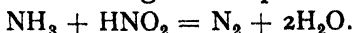


which is primarily the result of dissociation of nitric oxide



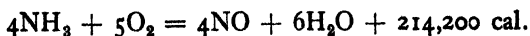
tends to take place if nitric oxide remains in contact with the catalyst unduly long. On the other hand,

at very high rates of flow there is difficulty in securing contact of the whole of the ammonia with the catalyst, so that some may escape oxidation ; this leads to a double loss, since the unchanged gas interacts with nitrous acid formed in a later stage of the process as follows :—



The condition necessary for a successful technical process is, therefore, mainly that oxidation of ammonia to nitric oxide should take place with maximum possible rapidity, all ammonia being completely oxidised, and none of the nitric oxide being further resolved into elementary nitrogen. In practice, using a platinum catalyst, a maximum efficiency of 95–97 per cent. can be obtained on a large scale, and the average efficiency of a modern plant is of the order of 92 per cent. conversion of ammonia to nitric oxide. Platinum catalysts are mainly used and are active from  $550^\circ$  upwards, the action being rapid at about  $700^\circ$ – $800^\circ$ , when the time of contact of gas with platinum is less than 0.001 seconds. The cheaper forms of non-platinum catalysts are active at about the same temperature, but the oxidation is somewhat slower, and a contact time of from 0.01 to 0.03 seconds is usually necessary.

With increasing temperature, the reaction proceeds still more rapidly, but formation of elemental nitrogen tends to increase. The temperatures referred to are really the average temperatures of the gas mixture near the catalyst surface, and the actual working temperature of the platinum gauze itself is usually about  $1,000^\circ$ – $1,025^\circ$ . Owing to the strongly exothermal nature of the action



the process can readily be made self-heating after an oxidation plant has once been started up.

#### The Platinum Catalyst Oxidation Process.

Platinum is employed in the form of very fine gauze, usually 80 mesh to the inch gauge made of

wire 0.065 mm. in diameter. When a new gauze is put into operation it is somewhat slow in action, but the activity gradually increases until a maximum is reached. At this stage it is seen that the gauze, originally smooth and bright, has become dull and grey in appearance, and if examined under the microscope, it is found that the whole surface is pitted and roughened in an extraordinary manner; this, of course, is an excellent illustration of the fact that the interacting gases come into direct combination with the catalyst during change.

The mode in which the catalyst is exposed to the gases varies somewhat. In Ostwald's original process<sup>5</sup> the converter consists of an internal nickel tube about 8 ft. long and 2 in. in diameter, surrounded by an outer tube of enamelled iron. The catalyst consists of a roll of crumpled platinum foil (about 50 gm.) mounted in the top of the nickel tube; the mixed gases enter the outer tube at the bottom, travel to the top and pass over the catalyst down the nickel tube, and serve to heat up the gases approaching the catalyst as they pass away to the exit. In the Frank-Caro process<sup>6</sup> the catalyst consists of a single rectangular layer of platinum gauze, 40 cm. by 60 cm., supported in an aluminium frame, between a lower aluminium vessel and an upper conical aluminium vent. Reference may also be made to the Kaiser apparatus,<sup>7</sup> in which the catalyst consists of several layers of platinum gauze placed close together across a tube of about 10 cm. diameter; in this process the air is pre-heated separately to about 300°, and only mixed with ammonia immediately before reaching the platinum gauze.

These earlier processes have been more or less standardised in various recent plants, and a brief description may be given of German, British and American practice.

Details have been given by Partington<sup>1</sup> of the ammonia oxidation plant of the Höchst Farbwerke of the I.G.



The catalyst consists of two to four circular platinum gauzes of the usual mesh, 20 in. in diameter, supported on grids of stout platinum wire in a cylindrical cast-iron converter, fitted with conical ends. The ammonia-air mixture containing one part of ammonia to seven of air is filtered through linen cloth and passed direct to the converters, each of which has an output of 1.5 tons of nitric acid per day. The gas from the battery of 224 converters passes to four rows of eight brick absorption towers (each 41 ft. high and 21 ft. diameter) packed with stoneware rings. The sources of the ammonia are synthetic cyanamide and coal-gas liquor. The oxidation efficiency is 89 per cent., and the overall efficiency (including absorption and concentration of nitric acid) is 84 per cent.

A good example of British practice is the ammonia oxidation plant of the United Alkali Company, described by Imison and Russell.<sup>3</sup> In this plant again a single layer of platinum gauze, 6 in. by 4 in. in size, is placed across a conical-shaped horizontal iron converter tube, the gauze being thus vertical. The converter is coupled to a tubular heat interchanger constructed of enamelled iron, or iron painted with a mixture of sodium silicate and barium sulphate. The ammonia-air mixture (one of ammonia to 7-9 of air) passes through the external part of the interchanger on its way to the platinum gauze, and its temperature is raised to about 300° by the heat of the oxidised gases passing through the internal tubes. The effect of pre-heating the gas mixture is to increase the efficiency of conversion to about 92 per cent. The main object of the United Alkali plants was to supply oxides of nitrogen for use in the chamber process of sulphuric acid manufacture; the method has proved exceptionally serviceable for this purpose, as it has been found to be far cheaper than the old nitre pots, both in costs of material employed and in the labour and supervision required. At the same time, increasing amounts of

nitric acid are being produced in Britain by this and other plants, the oxides of nitrogen being condensed and the acid concentrated as described below.

A description of American ammonia oxidation plants by Parsons<sup>2</sup> shows that the oxidation unit favoured is similar in general type to the British converter just described, but circular gauze cylinders are preferred to the flat gauze type, in that they are better adapted to large units and that it is easier to secure contact of all the ammonia with the gauze. The largest circular units in operation have a capacity of five tons of nitric acid per day. A recent patent of the Du Pont Corporation covers the passage of ammonia and air at 5-100 ft./sec. through 5-50 thicknesses of platinum or platinum alloy gauzes made from wire 0.003 in. in diameter.<sup>8</sup>

The main points of difference in the present-day converters having been indicated, a more general description of the various phases of the process may now be given.

*Sources of Ammonia.*—The only point which requires consideration as regards the origin of the ammonia is that of catalyst poisons. Phosphine, acetylene, hydrogen sulphide and silicon hydride may be present in traces in coal-gas ammonia or ammonia produced from cyanamide, and all these are toxic to a platinum catalyst. Since the cost of installation of the platinum gauze is an appreciable factor in the cost of the plant, it is necessary to make this, as far as possible, a capital charge, *i.e.*, the gauze must have a very long life and all catalyst poisons must be carefully removed. If synthetic ammonia from nitrogen and hydrogen is employed, catalyst poisons will probably be entirely absent. The other types of ammonia are best purified by scrubbing through strong caustic soda solution followed by passage over heated charcoal.

Another source of impurity which, according to Imison and Russell,<sup>3</sup> is more serious in its effects

than that of the gaseous compounds referred to, is the presence of iron oxide or other dust in the gas mixture, which settles on the catalyst gauze and impedes contact between the active surface and the interacting gases. Precautions are, therefore, always taken to filter the incoming ammonia-air mixture through layers of linen cloth and/or layers of fine mesh metallic gauze.

In general, ammonia liquor containing 20–27 per cent.  $\text{NH}_3$  from any of the three sources mentioned is the starting material. This is fed down a fractionating column at the base of which a current of steam and air is admitted; the amount of air is so regulated as to give the desired proportion of ammonia and oxygen in the gas escaping from the top of the column. It is found that the presence of a little moisture in the gas mixture is beneficial rather than otherwise as regards the efficiency of the conversion. The gas mixture is then purified as indicated above, and passes on to the converters or heat-exchangers.

The ammonia-air mixture producing plant should work, as far as possible, uniformly and almost automatically, delivering the mixture at a constant rate and constant in composition. After filtration from dust, the gas mixture should preferably only be exposed to aluminium, stoneware or enamelled (painted) iron plant in order to avoid picking up small particles of toxic metal oxides.

Practically all modern plants employ efficient heat-exchange systems between the oxidised gases and the air-ammonia mixture. As stated, Imison and Russell pre-heat the gas to about  $300^\circ$ , but other workers state that greater output (higher rate of flow of gas mixture) for a given efficiency can be obtained by pre-heating the gases to between  $460^\circ$  and  $500^\circ$ . It is probable that, so long as the gases are not at any time exposed to local temperatures greatly exceeding  $1,000^\circ$ , little falling off in efficiency of conversion takes place.

The use of oxygen and the efficient cooling of the reaction zone is the subject of a patent by Frank and Caro.<sup>9</sup> The mixture of 1 vol. of ammonia and 2-3 vols. of oxygen is passed through platinum or platinum-rhodium gauzes cooled by metal plates which are in turn cooled by boiling water. The catalyst is maintained at  $700^{\circ}$ - $1,000^{\circ}$  and a 95 per cent. conversion of ammonia to nitrogen peroxide of high concentration is claimed.

The cooled oxidised gases emerging from the heat-exchanger are dealt with in water or other absorption plants of the types about to be described.

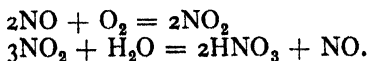
*Use of base-metal catalysts.*—Brief reference must be made to the use of mixed-oxide catalysts in place of platinum, a technique which has been developed to some extent in certain of the German factories, although it is probable that under normal conditions platinum is preferred for various reasons to these cheaper forms of catalyst. In 1871, Tessié du Motay<sup>10</sup> patented a process for oxidising an ammonia-air mixture at  $300^{\circ}$ - $500^{\circ}$  by passage over chromates, manganates or other similar salts. Modern developments of this idea in the hands of the German chemical companies<sup>11</sup> have taken the form of mixed-oxide catalysts, for example, mixed oxides of iron and bismuth, iron and copper, iron and cerium, iron and tungsten, or iron and lead.

Little definite information is available as to the actual composition of the mixtures proposed, but apparently an iron-bismuth oxide catalyst employed technically in Germany consisted of about 95 per cent. of iron oxide with about 3 per cent. of bismuth oxide. A Badische patent describes catalysts consisting of copper oxide admixed with smaller amounts of lead peroxide or manganese dioxide, which are capable of oxidising a 7 per cent. ammonia-air mixture with a yield of 90 per cent. of oxides of nitrogen. Scott<sup>12</sup> states that the best non-platinum catalyst consists of a mixture of 97 per cent. of cobalt oxide with 3 per cent. of bismuth oxide,  $\text{Bi}_2\text{O}_3$ . More recently, Adadurov and

Atroschtschenko<sup>13</sup> have claimed practically 100 per cent. oxidation of ammonia at 710°, using a mixture of silica, alumina and chromium oxide, to which a small proportion of cobalt nitrate had been added. These catalysts are employed in the form of a loose granular powder, and are active at about the same temperature as the platinum gauze catalyst, but operate considerably more slowly. It would also seem probable that the life of such catalysts would not be indefinitely prolonged as in the case of platinum gauze. The compactness and ease of operation of a platinum gauze catalyst unit are so marked that these features alone render the wide application of cheaper oxides unlikely, other than in exceptional circumstances.

#### Absorption of Nitric Oxide to Produce Nitric Acid.

In the case of ammonia oxidation the actual catalytic process is simpler and far more compact than the subsequent processes of converting the nitric oxide into nitric acid of commercial quality. This follows as a consequence of the two actions previously mentioned (p. 179), which are involved in the oxidation of nitric oxide to nitric acid :—



The oxidation of nitric oxide to nitrogen peroxide proceeds comparatively slowly ; for example, if the nitric oxide-air mixture contains 10 per cent. of the former gas, at least 2½ minutes is required for complete oxidation. A further complication is that in the conversion of nitrogen peroxide to nitric acid, one-third of the nitrogen is again liberated in the form of nitric oxide, which requires re-oxidation. We thus have an exceedingly fast ammonia oxidation process followed by relatively slow conversion of nitric oxide to nitric acid, and this is reflected in the technical plant by the necessary provision of absorption towers of very large size compared with the space occupied by the actual ammonia oxidation plant.

Further, in consequence of the slow and repeated oxidation which is necessary in the absorption towers, the concentration of the nitric acid finally produced tends to be on the low side and, as a rule, the strength of the acid from the towers is only about 50-55 per cent.  $\text{HNO}_3$ . Again, owing to the vapour pressure of mixtures of nitric acid and water, which are characterised by a minimum vapour pressure for an acid containing about 70 per cent.  $\text{HNO}_3$ , the final composition of the residue when dilute nitric acid is distilled is never more than 70 per cent.  $\text{HNO}_3$  (b.p.  $121^\circ$ ). Consequently nitric acid cannot be concentrated by straight distillation, and other methods have to be resorted to in order to produce 100 per cent. nitric acid.

The general principles adopted in the absorption of nitric oxide, or rather its oxidation to nitric acid, are to cool the oxidised gases from the ammonia oxidation converter in a gas-cooler, which may be constructed of aluminium or of chrome steel. In the course of cooling, the water produced in the original oxidation is separated to a large extent, and utilised later in the absorption towers. Efficient removal of the water present at this stage increases the concentration of nitric oxide and oxygen in the reacting gases, and favours the oxidation process. Some difference of opinion appears to exist with reference to the temperature at which the oxidation to nitrogen peroxide occurs most rapidly, but in modern practice this part of the process is generally conducted at as low a temperature as possible, that is to say, practically at atmospheric temperature.

The cooled gases are usually mixed with a further quantity of air (known as "secondary air") before passage to the absorption towers, which may be constructed of stoneware, acid-resisting bricks or acid-resisting metal. Special steels containing 18 per cent. of chromium or 18 per cent. chromium and 8 per cent. of nickel are now in fairly general use; these steels are entirely unaffected by nitric acid and also by atmospheric conditions. In view of the latter fact,

## SYNTHETIC NITRIC ACID

and of their good conductivity for heat as compared with stoneware, etc., this is a useful advantage in that the absorption towers may be exposed direct to the external atmosphere so that maximum removal of the heat evolved in the oxidation of the nitric oxide is secured.

The first absorption tower is usually empty, and serves simply as a chamber in which the initial oxidation of nitric oxide to nitrogen peroxide is effected as far as possible. The remaining towers are filled with packing material (which may consist of coke, Guttman balls or Raschig rings, etc.); the packing employed should expose a maximum of surface area per volume of material and at the same time should be such that when packed in the tower it leaves as large a free gas-space present as possible, so that the slow oxidation process may have every opportunity to complete itself in the gaseous phase.

In the towers a slow current of water trickles down over the surface of the packing, and meets the ascending nitrous gases, when the reactions previously referred to proceed, with regeneration of successively smaller concentrations of nitric oxide, which continues to be oxidised by the air present until at the exit from the last tower the process is practically complete. If the amount of water employed is controlled so that the average concentration of the nitric acid produced does not fall below 50 per cent., it is not possible to obtain complete absorption of nitrogen peroxide, and the final exit gases must be dealt with in some other way; usually this consists of final scrubbing through a tower containing dilute caustic soda solution, the final gases thus being converted into sodium nitrate.

It may be useful very briefly to illustrate the above by reference to various types of absorption plant.

For example, at the Höchst works (p. 182), the gases containing nitric oxide and steam pass through eight cast-iron mains, 18 in. in diameter, to four rows of eight absorption towers each, each row being provided

with twelve intensive coolers of special design, 5 ft. high and 2 ft. 6 in. in diameter, constructed in aluminium. The gas is passed through the coolers at high speed, and practically only water condenses, the condensate being used in the fifth absorption tower. The gases leaving the coolers at  $30^{\circ}$  are mixed with "secondary air" and passed through stoneware mains to the sets of absorption towers. The towers are constructed of brickwork, and are 41 ft. high and 21 ft. in diameter, packed with stoneware rings, leaving a total internal volume of about 35,000 cubic feet of gas space. This is distinctly on the low side, but at the Höchst factory 25 per cent. of the nitric oxide made is finally converted into nitrate of soda. The first towers are fed with water in order to produce nitric acid, which is obtained at an average concentration of 50 per cent., whilst the last two towers of the series are fed with saturated sodium carbonate solution in order to produce sodium nitrate. The efficiency of the whole absorption plant is said to be 97 per cent. The 50 per cent. tower acid is concentrated by mixing with sulphuric acid and de-nitrating as described below.

Imison and Russell's description<sup>3</sup> of the United Alkali Co. plant indicates that liquid nitric acid was produced by passage of the oxidised gases through stoneware towers, each 3 ft. in diameter by  $16\frac{1}{2}$  ft. high, the first of which was empty, the following three being packed with rings and fed with water, and the last two similarly packed, but fed with soda solution. This plant served to deal with the oxidised gases from a single converter with 6 in. by 4 in. gauze, and would produce about one ton of 100 per cent. nitric acid per week, the acid being actually obtained at about 50 per cent.  $\text{HNO}_3$ , whilst 5-6 per cent. of the total was in the form of sodium nitrate. The concentration of the 50 per cent. nitric acid was effected by heating with sulphuric acid in a de-nitrating tower of the usual type.

A description<sup>2</sup> of American practice indicates



that the absorption plant is constructed throughout of chrome steel, and comprises gas-coolers followed by a series of absorption towers, comparable in proportions with those used in Germany. Fifty to 57 per cent. nitric acid is obtained from the water-absorption towers, and in the final tower of the system, constructed of ordinary steel, the 2-3 per cent. of the total nitric gases which have escaped absorption as dilute nitric acid are converted into sodium nitrate by means of sodium carbonate solution. The absorption efficiency is of the order of 95-96 per cent.

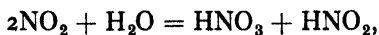
#### Production of Concentrated Nitric Acid.

The general method employed for concentration of the 50 per cent. acid produced in the absorption towers consists in mixing, say, seven parts of the dilute acid with one part of concentrated sulphuric acid and distilling the mixture from a cast-iron pot-still. The process may be made continuous by employment of a de-nitrating tower, which is practically an acid-resisting fractionating column, filled with acid-resisting packing and fed with a constant stream of concentrated sulphuric acid. The 50 per cent. dilute nitric acid is vaporised into the base of the tower and passes up through the descending sulphuric acid. The result is that the water is transferred from the nitric acid to the sulphuric acid, and nitric acid of 96-97 per cent. strength distils away from the head of the tower and is condensed in aluminium or chrome steel pipes and, if necessary, finally passed down a small stoneware tower, where it meets a current of compressed air, which removes any residual oxides of nitrogen.

The diluted sulphuric acid leaving the base of the de-nitrator is re-concentrated (for example, in a Gaillard tower) and used again.

Other suggestions have been made in order to avoid the somewhat elaborate de-nitration process. For example, Meister, Lucius and Brünig<sup>14</sup> have taken out patents for enriching 60 per cent. nitric acid

obtained in absorption towers with nitrogen peroxide, and submitting the solution obtained to the action of oxygen, with the result that the action



followed by oxidation of most of the nitrous acid to nitric acid takes place, and consequently the concentration of the acid is considerably increased. A patent by Cederberg<sup>15</sup> indicates that, if no water other than that formed in the original oxidation of ammonia is present, it is possible to effect absorption of the nitric oxide in such a way that a 70 per cent. acid is produced.

If it were possible to obtain 100 per cent. nitric acid by simple distillation the synthetic nitric acid process would be much simpler and exceptionally efficient. It is, of course, possible to produce larger proportions of the acid from the oxidised gases in the form of sodium nitrate or, for example, of calcium nitrate, and where metallic nitrates are required as such for fertilisers, etc., this is simple and convenient. So far as the production of the concentrated acid is concerned, however, it is obviously uneconomic to have recourse to the intermediate production of sodium nitrate, which would again involve distillation with sulphuric acid and production of the practically waste nitre cake (acid sulphate of soda) as by-product.

There has been a tendency in recent years towards the employment of increased pressure for the production of concentrated nitric acid. Fauser<sup>16</sup> described a process for the oxidation of ammonia under 5 atmospheres pressure, which was successfully carried out on a semi-technical scale (10 tons of nitric acid per day). Although the rate of oxidation was but little accelerated, great economy was effected in ground space and steam for heating, whilst the most important feature is that 74-75 per cent. nitric acid could be directly produced. It is, however, considered preferable to carry out only the further oxidation of the nitric oxide

under increased pressure; for, according to Fauser,<sup>16</sup> the efficiency of oxidation of ammonia, other things being equal, is reduced by increase of pressure, and at 4 atmospheres not more than 91 per cent. conversion is attainable, and the life of the catalyst is much shorter. This author recommends a gas mixture enriched with oxygen and carries out the ammonia oxidation at ordinary pressure and at 850°-950°. The gases are then compressed in chromium-steel turbo-compressors to 3-3.5 atmospheres and are scrubbed with dilute nitric acid in a counter-current manner in horizontal steel cylinders externally cooled with water; 12 cylinders give 95 per cent. absorption and 19 cylinders 99 per cent. absorption. Use of increased pressure is said to be twice as economical in power as the use of artificial cooling.

The Du Pont de Nemours Corporation have patented the use of increased pressure during the further oxidation of nitric oxide and its absorption in dilute nitric acid.<sup>17</sup> This procedure has been further discussed by Fauser,<sup>18</sup> who proposes to produce concentrated nitric acid by using oxygen at high pressures. The gases from the oxidation of ammonia are cooled, thereby removing the bulk of the water vapour as dilute nitric acid. The remaining gases are then compressed to 8-10 atmospheres and passed counter-current to a stream of dilute nitric acid in an oxidation tower maintained at -10°. The mixture is then treated with oxygen at 70° and 50 atmospheres pressure, yielding 98 per cent. nitric acid as the product. A somewhat similar process has been patented by the Lonza Elektrizitätswerke und Chemische Fabriken A.-G.<sup>19</sup>

When the costs of compression, artificial cooling and oxygen are considered, it seems doubtful whether the entire elimination of the use of sulphuric acid and distillation plant in such processes constitutes much of a financial advantage



## CHAPTER VII

### THE SULPHURIC ACID INDUSTRY

SULPHURIC acid has been manufactured for nearly 200 years by one or other of two alternative catalytic processes. The older process, known as the chamber process, goes back to somewhat before 1750, and is extremely interesting from a theoretical standpoint, because it is one of the very few cases in which catalytic action proceeds (to a certain extent, at all events) in a homogeneous gaseous system; the earliest explanation of the processes operating in the sulphuric acid chambers was given by Sir Humphry Davy about 1812. The greater part of the world's production of sulphuric acid is still carried on by the chamber process, but during the past fifty years the contact process, which consists of interaction of sulphur dioxide and atmospheric oxygen at the surface of a solid catalyst, has developed considerably, especially in conjunction with the manufacture of fuming sulphuric acid, technically known as oleum.

For the sake of compactness, both processes of sulphuric acid manufacture will be considered in the present chapter, although only the modern contact process belongs strictly to the heterogeneous type of catalytic action with which we are concerned in the present Section of this book. For the latter reason, and also in order to bring the catalytic oxidation of sulphur dioxide more closely into relationship with the oxidation of ammonia described in the previous chapter, the contact process will be dealt with before describing the older chamber process; the latter, although it is a case of homogeneous catalysis in

either a gaseous or a liquid system, forms the subject of the concluding part of the present chapter.

Before proceeding to describe either process, however, it is well to glance at the general conditions of the sulphuric acid industry at the present day, and also to consider the various sources from which sulphur dioxide is at present obtained for use in either process.

A statesman of the Victorian era is reported to have said: "Show me the state of the sulphuric acid industry, and I will tell you the state of trade in England." At the period in question, sulphuric acid was necessary for the manufacture of alkali by the Leblanc method, for the production of phosphate manures from bone for agriculture, for the extraction of various metals, and for very many other purposes; so that to a large extent, sulphuric acid was indeed the backbone of the chemical industries, and therefore indirectly of an important part of the manufacturing trades of the country. It is pleasant to reflect that even in the middle of last century a politician was to be detected who seems to have realised that chemicals form the foundation of the world's industries.

At the present time matters have altered considerably, and probably permanently, for sulphuric acid is being displaced in several industries from its former position as an integral agent in the manufacture of various compounds. Thus, phosphoric acid is beginning to be produced from natural phosphates by volatilisation methods, leading to the production of phosphatic nitrogen fertilisers in which calcium superphosphate (made by the action of sulphuric acid) is absent. Again, the Leblanc soda-ash process is on the verge of extinction, at all events in this country, and alkali is now made either by the ammonia-soda method or electrolytically. Both by-product ammonium sulphate and nitric acid from Chile nitrate involved the use of sulphuric acid; the new methods of obtaining fixed nitrogen are tending more

and more to dispense with the use of sulphuric acid altogether. Although at an early stage synthetic ammonia was absorbed in solutions of free sulphuric acid, present practice almost invariably favours the double decomposition of ammonium carbonate with a suspension of natural calcium sulphate, and it is quite likely that the by-product ammonia producers will follow the lead of their synthetic competitors and adopt a similar system for conversion of the coal-gas ammonia into sulphate. Similarly, the catalytic method of producing nitric acid requires sulphuric acid only during the concentration of the nitric acid solutions produced, and the concentration process requires make-up sulphuric acid only to replace mechanical losses.

On the other hand, although these important industries have tended to eliminate sulphuric acid to such a large extent, it must not be forgotten that many industries, such as the manufacture of organic chemicals, dyestuff intermediates, artificial silk, are expanding steadily, and in some cases rapidly, and that sulphuric acid must always be an important reagent in manufacturing processes of these and other kinds. Furthermore, certain new uses for sulphuric acid are being developed. Thus, in the spring of 1935, 29,000 acres of cornland in this country were sprayed with 1,620 tons of commercial sulphuric acid (B. O. V.) in a diluted form for the eradication of charlock and other annual weeds, and in 1934, 4,000 acres of potato crop were similarly treated to destroy the haulm, thus preventing the possibility of disease spreading down to the tubers and facilitating the harvesting of the crop. Therefore, although it is quite possible that the production of sulphuric acid has reached something approaching its maximum, it is not likely that the demand for this acid will fall off to a very great extent under normal conditions of trade.

Some figures illustrating the production of sulphuric acid in recent years may now be given :—

*Production in Great Britain, 1913-1935.*

	Tons (100 per cent. $\text{H}_2\text{SO}_4$ )
1913 . . . . .	1,150,000
1917 . . . . .	1,382,000
1921 . . . . .	561,000
1924 . . . . .	890,000
1928 . . . . .	928,000
1929 . . . . .	967,000
1930 . . . . .	850,000
1934 . . . . .	886,000
1935 . . . . .	936,300

*Production in the U.S.A.*

1913 . . . . .	2,200,000
1928 . . . . .	4,010,000

In England the bulk of the acid is still produced by the chamber process; thus, of the acid produced in the first six months of 1935, 75 per cent. was chamber acid and 25 per cent. contact acid. The present production of contact acid in this country is therefore of the order of 240,000 tons per annum. A similar state of affairs holds in other countries. Thus, of the four million tons of acid produced in the U.S.A. in 1928, 71 per cent. was made by the chamber process.

**Technical Sources of Sulphur Dioxide.**

The chief sources of sulphur dioxide, which is the raw material for sulphuric acid, include iron pyrites, elemental sulphur, spent iron oxide, natural calcium sulphate (gypsum or anhydrite), other metallic sulphides such as zinc blende or copper ores, and spent alkali waste.

Until comparatively recent times, the main source of the gas was iron pyrites, especially Spanish pyrites, which usually contains about 3-4 per cent. of copper as sulphide. The pyrites is heated in a current of air at about  $400^{\circ}$ - $500^{\circ}$  in furnaces or "burners," which are usually mechanically operated. The older reverberatory type of burner<sup>1</sup> has long been replaced by rotary furnaces of the MacDougall, Herreshoff or



other types,<sup>2</sup> consisting of a vertical cylinder with fixed horizontal trays, furnished with a central shaft carrying rotary scrapers. Inclined rotary kilns somewhat similar to a cement kiln are also used in some installations. The saving of labour accomplished by the use of mechanical burners is to some extent mitigated by the production of considerable amounts of flue dust in the exit gases, although this is minimised by employing only natural draught for the gases in the ovens. It is necessary, however, to pass the pyrites-gases through large chambers fitted with baffles which act as dust separators, in order to produce sufficiently clean gas for the operation of the chamber process. Even this provision is not enough to cleanse the gases adequately for use in the contact process, for they still contain minute suspended particles of ferric oxide, and especially of arsenious oxide,  $As_4O_6$ , which are strongly toxic to the platinum catalysts employed. Further purification (although still not sufficient for purposes of the contact process) is effected in modern pyrites-burning plants by the installation of a Cottrell electrostatic dust precipitation plant, through which the flue gases are led.

Recently a new type of pyrites burner has been introduced, known as the Bracq-Laurent burner,<sup>3, 4</sup> which consists of a sloping hearth constructed of refractory material carrying a layer of pyrites, which is raked forward by moving arms which describe elliptical movements owing to the rotation of a central shaft to which they are fitted. The shaft is rotated alternately in either direction, and the result of the motion is to produce in the pyrites a series of trenches which are successively swept forwards in a downward direction. The result of this method of raking the pyrites is to tend to keep it at the surface of the hearth and to minimise dust formation. In fact, it is stated that the operation of this burner at several Continental works has justified the designers' claims that its employment dispenses with the necessity for any dust

separator, so far as the production of chamber acid is concerned.

In cases where spent iron oxide from gas works is the source of the sulphur dioxide, the burners employed are somewhat similar to those used for pyrites.

It should be noted that the oxidation of iron sulphide is a burning rather than a roasting process, that is, once the oven has been started by the use of a few spadefuls of red-hot coke, oxidation of the pyrites proceeds exothermally and continuously.

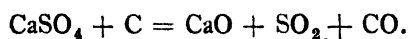
An increasingly important source of sulphur dioxide is elemental sulphur, which is now obtained largely from the West Indies, Texas and other parts of the southern United States from subterranean deposits of natural sulphur. This is usually extracted by the Frasch process, in which a shaft is drilled into the deposit and fitted with an internal aluminium pipe. Steam at about 100 lb. pressure is passed down the external shaft until a sufficient quantity of the sulphur deposit is melted; the steam is then replaced by compressed air, which forces the fused sulphur and hot water up the central tube, at the outlet of which the sulphur is collected in large tanks and obtained in a condition of over 99 per cent. purity.

Native sulphur of this kind is usually burnt in a stationary furnace on layers of iron trays, the furnace being supplied at the base with a current of air; rotary furnaces are also employed. The design of an efficient sulphur burner is more difficult than that of a pyrites burner because temperature control is much more important; it is necessary to avoid overheating, since, in addition to obtaining too rapid fusion of the sulphur it is easily possible to lose sulphur by distillation and sublimation.

Sulphur obtained from alkali waste by the Chance process (this Section, Chapter IX, p. 235) was formerly used to some extent in sulphuric acid manufacture, and was burnt in ovens of design similar to those now used for native sulphur.

An appreciable proportion of sulphur dioxide is also obtained, especially in America, Germany and Belgium, from the roasting of zinc blende and nickel-copper sulphide ore residues. The temperature necessary to convert this class of sulphides into oxides is considerably higher than in the case of iron pyrites, namely, about  $800^{\circ}$ – $900^{\circ}$ . The operation is carried out in a closed or muffle furnace, which consists, in the Hasenclever type,<sup>5</sup> of a number of horizontal furnaces completely enclosed in a series of horizontal flues for the heating gases. By means of another series of flues passing through the interior of the muffles, hot air is passed over the surface of the ore. The fuel consumption required in treating these ores is, of course, much greater than in the case of pyrites burning and amounts to about 15–20 per cent. of the weight of ore treated. The cost of this fuel is balanced, however, by the higher value of the residual metals (zinc, copper, or nickel) which are subsequently extracted from the calcined ore.

Finally, processes have recently been developed in Germany<sup>6</sup> for the conversion of gypsum or anhydrite into sulphur dioxide and Portland cement, depending on the primary action



The operation is carried out in a rotary kiln in which the powdered mineral meets a current of pulverised fuel. In order to recover the lime in an economic form, the mineral calcium sulphate is first intimately mixed with clay and the mixture dried before entering the kiln. An oxidising atmosphere is maintained in the kilns, so that the carbon monoxide formed is converted to carbon dioxide during the process, and also formation of carbon oxysulphide or calcium sulphide is minimised. The cement produced is ground with blast-furnace slack and sold as blast-furnace cement, whilst the exit gases from the kiln contain 6–7 per cent. of sulphur dioxide, and are washed and passed through a

Cottrell electrical separator, when they are ready for use in the manufacture of sulphuric acid either by the chamber or the contact process. It is understood that the production of sulphuric acid and cement from anhydrite is being carried on in this country at the present time on a large scale.

The following table shows the general composition of gas mixtures produced by the above methods.

Name of Mineral.	Percentage Sulphur Dioxide.	Percentage Oxygen.	Percentage Nitrogen.
Pyrites. . .	7-8	6-11	81-87
Sulphur . . .	10-11		
Blende. . .	9	8	83
Gypsum . . .	6-7	6-10	83-88

For many purposes, such as for electrical accumulators, or for use in connection with edible products, such as invert sugar, fats, glycerine, etc., it is imperative that the sulphuric acid employed should be entirely free from arsenic. Whilst, as indicated later (p. 219), it is possible to remove traces of arsenic quite efficiently and fairly cheaply from the finished sulphuric acid, it is also of considerable advantage in such cases to employ raw material which is practically arsenic-free; in other words, in the production of arsenic-free acid it is desirable to use sulphur dioxide prepared either from pure native sulphur or by the gypsum process.

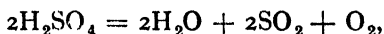
In conclusion, it may be of interest to indicate the proportion of acid obtained from various sources in this country in recent years.

*Sources of Sulphuric Acid (per cent. of Total)*

	Pyrites and Anhydrite.	Spent oxide.	Sulphur and H <sub>2</sub> S.	Zinc ores.
1934 . . . . .	52.67	24.87	14.01	8.95
1935 (January to June) . . . . .	51.96	21.85	15.51	10.68

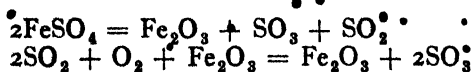
**The Contact Sulphuric Acid Process.**

This method, which consists in passing a mixture of sulphur dioxide and oxygen over a catalyst which may be either composed of platinum or of oxides of iron and certain other metals, is obviously similar in general principles to the Kuhlmann process of oxidation of ammonia to nitric acid. Like the latter, the possibility of carrying out this reaction was known for many years before means were found to put it into technical practice. Sir Humphry Davy, in 1812, suggested that spongy platinum might serve as a catalyst in the production of sulphur trioxide, and in 1831, a patent was actually taken out by Phillips<sup>7</sup> for this process, but technically it was a failure, as the platinum invariably rapidly lost its power of effecting the oxidation. The method was allowed to lapse for nearly fifty years, until Squire and Messel,<sup>8</sup> in 1875, succeeded in maintaining the activity of the platinum on a commercial scale, by employing mixtures of sulphur dioxide and oxygen prepared in a special manner; they either produced the mixture from concentrated sulphuric acid by passage over red-hot firebrick :—



or by burning specially purified sulphur in air. The gases were dried by means of sulphuric acid and then passed over finely-divided platinum and absorbed in strong sulphuric acid, thus producing the so-called fuming acid,  $\text{H}_2\text{S}_2\text{O}_7$ .

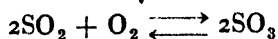
At the period in question the demand for fuming sulphuric acid (oleum) was growing considerably with the rapid expansion of the synthetic dyestuffs industry, where it was required in many processes of sulphonation and nitration. The only source of this acid prior to Squire and Messel's process was distillation of ferrous sulphate in a current of air by the old Nordhausen process :—



This explains why Squire and Messel's process, which, starting from sulphuric acid, at first sight seems to be uneconomic, became a profitable source of oleum,  $\text{H}_2\text{S}_2\text{O}_7$ , for many years.

Naturally, however, attempts continued to be made<sup>9</sup> to utilise the platinum oxidation process for the ordinary sulphur dioxide-air mixture produced, for example, from pyrites burners, and the German dyestuff companies, especially the Badische Company and Meister, Lucius and Brünig, investigated the process both from the point of view of general physico-chemical considerations and also with reference to rapid poisoning of the catalyst. This work led to the production of contact sulphuric acid on the large scale in Germany towards the end of the nineteenth century.

It should again be pointed out, however, that although the contact process has reached a very high state of efficiency, the older chamber process is also highly efficient and economical in working, and still has the advantage over the contact process so far as production of ordinary commercial oil of vitriol is concerned. The chief technical value of the contact process lies in its utility as a source of oleum, which is used not only in sulphonation and nitration processes of the dyestuffs industry, but also in the nitration of cellulose for the production of explosives, celluloid, etc., and in the recovery of waste nitric acid from these and other nitration processes. The detailed study of the action



was mainly carried out by Knietzsch<sup>10</sup> and his collaborators, who showed that higher percentages of sulphur trioxide in the equilibrium mixture would be realised the lower the temperature, that the temperature should preferably be maintained at or below  $450^\circ$ , and that the yield of sulphur dioxide is increased with increasing concentration of oxygen in the original gas mixture, subject to the restriction that undue dilution owing to the presence of atmospheric nitrogen again

tends to reduce the yield. Maximum working yields are obtained when the oxygen is present in three times the theoretical amount demanded by the above equation, that is, two volumes of sulphur dioxide to three volumes of oxygen or fifteen volumes of air. Under the latter conditions 98 per cent. conversion to sulphur trioxide is obtained at  $400^{\circ}$ – $450^{\circ}$  as against 91 per cent. conversion employing the theoretical amounts of sulphur dioxide and air. Other physico-chemical data dealing with this reaction are to be found in the subsequent work of Bodländer,<sup>11</sup> Bodenstein<sup>12</sup> and their collaborators.

The second and more vital problem for the commercial success of the process, namely, the removal of impurities toxic to the catalyst, was also successfully solved. It has been indicated that Squire and Messel, realising that the source of the catalyst poisons lay in the pyrites gases, employed purer forms of sulphur dioxide-oxygen mixtures. Knietsch and Krauss<sup>10</sup> established definitely that the actual poison was the dust contained in the pyrites, mainly ferric oxide, which also contained appreciable traces of arsenic and selenium, both strongly poisonous to catalytic platinum. If these impurities were carefully removed by drastic scrubbing processes to such an extent that they exhibited no fog in a strong beam of light, the platinum was found to maintain its activity at a constant value almost indefinitely. The actual form of gas purification adopted on the large scale by the Badische Company consisted in injecting atomised steam into the gases from the pyrites burners, followed by cooling to  $100^{\circ}$  in a lead condenser, and scrubbing in a series of towers with water, after which the gases were passed through a tower scrubber containing strong sulphuric acid.

It should be mentioned that in the course of Knietsch's comprehensive investigation of the process it was found that in addition to platinum distributed on various supports (for example, pumice, firebrick,

asbestos), oxides of iron, chromium, vanadium and similar metals, including a number of the oxides of the rare earth metals, were also more or less efficient as oxidising catalysts. The catalysts of the oxide class, however, operate at considerably higher temperatures, namely, about  $700^{\circ}$  instead of  $400^{\circ}$ – $450^{\circ}$ , and under these conditions the percentage of sulphur trioxide in the equilibrium mixture is only of the order of about 60 per cent. The latter type of catalyst, in the form of ferric oxide, nevertheless has an advantage in that passage of pyrites-burner gases over a mass of burnt pyrites (that is, ferric oxide containing traces of other oxides) at about  $700^{\circ}$  has the double effect of removing flue dust and fixing all arsenic and similar impurities, whilst at the same time about 60 per cent. conversion to sulphur trioxide is also achieved. This procedure is therefore utilised in what is known as the Mannheim contact process,<sup>13</sup> in which gas purification and considerable production of sulphur trioxide is secured simply by passage of the original gas mixture through ferric oxide, the conversion to sulphur trioxide being completed by subsequent passage over platinum catalyst.

Catalysts containing one of the oxides referred to above, namely vanadium pentoxide, have been the subject of much research in the last ten years or so, and as a result, mainly of the work of Jaeger, Bertsch and the Selden Co. of America,<sup>14</sup> the use of these catalysts for the production of sulphuric acid by the contact process has become firmly established. The catalyst favoured by the Selden Co. takes the form of a non-siliceous base-exchange zeolite containing vanadium pentoxide in the non-exchangeable nucleus. The material may be diluted with porous substances such as kieselguhr, or may be coated on to massive granular fragments of ferrous alloys, quartz, etc. With burner gases containing 5–9 per cent. of sulphur dioxide, 97–99 per cent. oxidation is claimed.<sup>15</sup> These catalysts are very resistant to heat treatment, and



possess long life and immunity towards the gaseous poisons which adversely affect platinum catalysts.

We now proceed to describe the main forms of the contact process, namely, the Badische, Grillo, Mannheim and the vanadium pentoxide processes.

*The Badische Contact Process.*—The Badische converter consists of a fairly large cylindrical iron vessel, in the interior of which a number of vertical iron tubes are set, somewhat in the form of a tubular condenser. The inner tubes are packed loosely with asbestos fibre on which 10 per cent. of platinum has been deposited, usually by impregnation with platinum chloride followed by reduction with an alkaline formaldehyde or formate solution.

The mixture of sulphur dioxide and air from the pyrites or other burners, containing as a rule about 7 per cent. sulphur dioxide and 10–11 per cent. oxygen, has been purified by intensive cooling and scrubbing as described above, and enters at the base of the external iron converter and passes upwards, where it is directed by an arrangement of baffle flues into the tops of the interior catalyst tubes, which are maintained at  $400^{\circ}$ – $450^{\circ}$ . The oxidised gases enter a common flue at the base of the catalyst tubes and pass away to a series of sulphuric-acid towers, in which the sulphur trioxide is absorbed so as to produce oleum, usually containing 60 per cent. sulphur trioxide.

The action  $2\text{SO}_2 + \text{O}_2 = 2\text{SO}_3 + 21,700^{\circ}$  cals. is sufficiently exothermic to allow the process to proceed without external heat once it has been set going. It is important, in order to secure total conversion, to ensure that the temperature of the catalyst does not rise above about  $500^{\circ}$ , and this is aided by a system whereby the entering gases are admitted not only at the base of the converter as described, but can also enter at one or more other points higher up the converter. Thus, by controlling the intake of the purified gas mixture, the temperature in the catalyst tubes can be closely regulated.

*The Grillo Process.*<sup>16</sup>—This is generally considered to be the most efficient form of the contact process. It is distinguished from the other processes by the employment of a special form of platinised magnesium sulphate as catalyst; this is prepared by impregnating the ordinary hydrated sulphate,  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ , with a solution of platinum chloride and placing the dried impregnated material on a number of superimposed iron trays set in a vertical converter, heated initially by flue gases and, subsequently, by a process of heat exchange somewhat similar to that used in the Badische converter. On heating the impregnated magnesium sulphate in a current of sulphur dioxide and air the anhydrous salt is produced in a somewhat voluminous bulky form, whilst at the same time the platinum salt is decomposed and the metal set free. The extensive surface thus produced causes this form of catalyst to be highly active with reference to the space occupied; for example, it is possible to produce one ton of oleum per day from about 1.75 kg. of catalyst containing not more than 5 gm. of platinum.

The gases, before entering the converter, are purified in the same manner as in the Badische process, and the plant is so worked that a temperature of  $400^\circ$  or somewhat less is maintained in the converter; the exit gases from the converter are absorbed in concentrated sulphuric acid as in the former case.

*The Mannheim Process.*<sup>13</sup>—This is designed on somewhat different lines from the two preceding processes, and was worked out by Clemm and Hasenbach at about the same time (1898) as the first Badische processes came into operation. As already stated, the oxidation is conducted in two stages, in the first of which ferric oxide is employed both as a preliminary catalyst and also in order effectively to purify the crude pyrites-burner gases.

The installation is somewhat complicated, but consists essentially of a set of suitably designed pyrites burners, the gases from which enter an oven in which

burnt pyrites, which has already been used as a source of sulphur, is heated to  $600^{\circ}$ – $700^{\circ}$  on a revolving hearth. The gases from the burners pass upwards through the red-hot burnt pyrites, and some 50–60 per cent. of the sulphur dioxide is converted to trioxide, whilst the dust impurities, etc., are being removed. The exit gases are scrubbed through strong sulphuric acid, which removes the sulphur trioxide already formed, and are then passed through coke scrubbers to remove sulphuric acid mist, and proceed to the platinum converter, which is maintained at about  $450^{\circ}$  and contains platinised asbestos.

*The Vanadium Pentoxide Process.*—The following <sup>17</sup> is a brief description of a recently erected American plant which employs the Selden Co.'s vanadium catalyst. Sulphur is melted by steam in brick-lined pits and pumped to stationary burners consisting of vertical steel cylinders lined with fire-brick, filled with chequer work and provided with primary and secondary air ducts. The gases are cooled in a cast-iron shell surrounded by an outer steel shell, and after dust removal pass to two cast-iron converters placed in series. The first converter effects 80 per cent. conversion and the second, a further 16.5–17 per cent. The vanadium pentoxide catalyst in granular form is packed on iron screen shelves interspersed with iron baffles. Absorption of the sulphur trioxide takes place in a steel tower lined with acid-resisting bricks and packed with rings. The plant covers a floor space of 112 square feet per ton of sulphur oxidised per day, and can be handled by one operator.

It is difficult to say which of these processes is the most efficient in actual working; the compactness of the Grillo installation and the combined purification and partial conversion of the Mannheim process are points in favour of these, both of which were operated by the Ministry of Munitions in this country during the war of 1914–1918. The general conclusion of the Ministry was that the Grillo process was on the whole

the most efficient and economical under the conditions then obtaining. In 1933, it was stated that in the U.S.A. the Grillo process was still employed in small plants, that no Mannheim plants existed, and that the larger contact plants had been adapted for use with vanadium catalysts.

There has been much discussion concerning the relative merits of the vanadium and platinum catalysts. It appears that vanadium catalysts do not operate satisfactorily with gases containing much more than 8 per cent. of sulphur dioxide, owing to the large excess of oxygen (200–300 per cent.) required to prevent reduction of vanadium pentoxide to lower oxides with consequent loss of activity. At equal space velocities, platinum will operate satisfactorily over a greater temperature range than vanadium. The former also has a greater "overload" capacity than the latter. Vanadium catalysts, on the other hand, are robust and resistant to poisons. Then again, although the initial cost of the vanadium is only one quarter that of platinum, the return value of the latter is disproportionately higher. As regards the position in this country, it was stated<sup>18</sup> in 1932 that "in the light of the experience in this country at the present time, when the low price of platinum and the royalties on the vanadium catalysts are taken into account, the economic advantage is on the side of platinum."

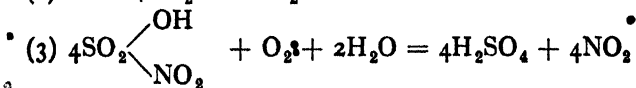
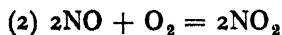
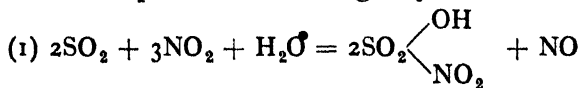
The restriction of the contact process to the production of oleum seems at first sight to be unnecessary since, assuming that working costs permitted, it is evident that the ordinary concentrated acid or "monohydrate"  $\text{H}_2\text{SO}_4$  should be produced by absorption of the sulphur trioxide in water instead of employing strong sulphuric acid. The technical objection to this procedure is that it is almost impossible to absorb the suspension of solid sulphur trioxide in the exit gases by means of water. The sulphur trioxide mist, in spite of the strong mutual attraction between sulphur trioxide and water, is only very partially

absorbed when the gases containing it are exposed to the action of water, even in an efficient scrubbing plant. As the older chamber process is equally economical to run and gives highly efficient conversion of sulphur dioxide to sulphuric acid, it is probable that the contact process will be restricted to the production of the fuming acid.

**The Chamber Sulphuric Acid Process (a Case of Homogeneous Catalysis).**

The operation of the chamber process is so thoroughly dealt with in numerous monographs, and is also so familiar to the most elementary student of chemistry, that its formal description may be replaced in the present book by consideration of (1) the catalytic actions which take place, and (2) the modern modifications introduced into the process with a view to economy of chamber space and efficient concentration of the Glover acid.

The process dates from about 1740, lead chambers being first introduced by Roebuck in 1746. It was not until about thirty years later that steam was supplied to the chambers in addition to the mixture of moist sulphur dioxide and nitrous gases from the pots. At the close of the 18th century, Clément and Désormes investigated the process and indicated the main reactions which took place, and in 1812 Davy put forward the view that the nitrogen oxides were concerned in the transformation of sulphur dioxide to trioxide, and suggested that the process could be summed up in the following way:—



The vital parts of a chamber plant are the Glover tower, the chambers and the Gay-Lussac tower.

The reactions referred to take place almost entirely in the chambers and (in the older types) to a considerable extent in the gaseous phase; but it seems probable that part of the oxidation always occurs in the liquid phase in aqueous solution either as mist or on the walls of the chambers. The main function of the Glover tower is to concentrate the relatively weak acid produced in the chambers, and at the same time to eliminate therefrom dissolved oxides of nitrogen; it is, therefore, worked on the counter-current system, chamber acid flowing down the tower and meeting a stream of air from the pyrites burners containing 6-12 per cent. of sulphur dioxide together with a certain amount of oxides of nitrogen produced from nitre pots, or in modern plants by oxidation of ammonia. The hot gases concentrate the chamber acid from about 65 per cent. to 78 per cent. (commercial oil of vitriol), carry forward with them oxides of nitrogen dissolved in the chamber acid, and are simultaneously cooled to the working temperature of the chambers.

The Gay-Lussac tower, which, like the Glover tower, is packed with earthenware balls or hard coke, is connected with the gas exit of the chambers and fed with a slow stream of concentrated sulphuric acid. The result is that any oxides of nitrogen passing away with the nitrogen and other spent gases are absorbed with production of the so-called nitrous vitriol, the main component of which is nitro-sulphonic acid,  $\text{SO}_2(\text{OH})\text{NO}_2$ . This tower is maintained at a temperature of about  $30^\circ$ - $40^\circ$ , a higher temperature leading to the decomposition of the nitro-sulphonic acid. The volume of the Gay-Lussac tower should be at least one per cent. of that of the chamber space, and frequently in modern works two Gay-Lussac towers are installed in series.

The Gay-Lussac tower is constructed of masonry lined with sheet lead, and is usually 32-50 ft. high by 4-10 ft. wide. The Glover tower is similarly lined

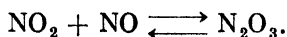
with very stout lead and fitted with an internal lining of acid-resisting bricks; acid-resisting stoneware is the usual packing employed in this tower, which is about 25–30 ft. high by about 6 ft. in diameter. In addition to the chamber acid, nitrous vitriol from the Gay-Lussac tower is also supplied at the head of the Glover tower, and the upper part of this tower is mainly concerned in de-nitrating the sulphuric acid according to the reaction



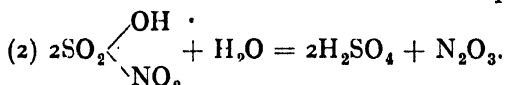
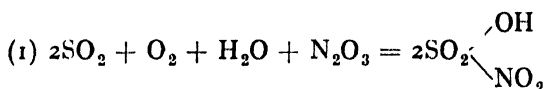
In modern plants this process accounts for as much as 25–30 per cent. of the total output of sulphuric acid. At the same time the burner gases, as already stated, are cooled to the chamber temperature in the upper part of the Glover tower and also carry with them aqueous vapour, removed from the sulphuric acid, which forms part of that required for the chemical action proceeding in the chambers. The function of the lower part of the Glover tower is almost exclusively concentration of the sulphuric acid by means of the hot burner gases.

Coming now to the part of the plant in which the main catalytic action is carried out, namely, the chambers, and confining our attention in the first place to the old-fashioned type in which the necessary amount of water vapour was made up by injection of steam, the chambers were usually about 100–130 ft. long by 20–30 ft. diameter and 15–25 ft. high. Each unit was constructed of pure lead sheets supported on a wooden framework, and, as a rule, three, or sometimes four of them, were connected in series. The reactions proceeding in the chambers have formed the subject of many detailed investigations<sup>19</sup> since the original work by Davy and by Clément and Désormes, the most informative being that of Lunge and Naef, published between 1884 and 1890. In presence of insufficient moisture in the chambers, a deposit of solid “chamber crystals” takes place,

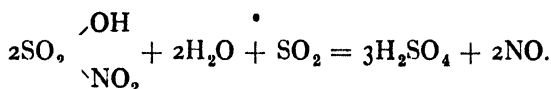
these consisting of Davy's nitro-sulphonic acid. Lunge and Naef carried out an exhaustive examination of the composition of the gases in each chamber, and found that after the first (in which the gases were colourless) the oxides of nitrogen present were coloured and consisted of equimolecular proportions of nitric oxide and nitrogen dioxide, which behaved as  $N_2O_3$  :—



They therefore modified Davy's conception of the chamber processes by assuming that the actual catalyst, so to speak, was  $N_2O_3$  rather than alternately  $NO_2$  and  $NO$  as in Davy's explanation :—



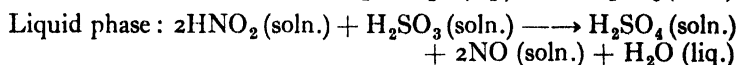
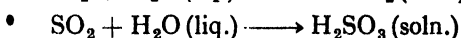
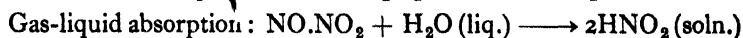
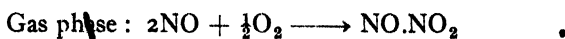
The observation that the gases in the first chamber, when the process is working efficiently, are colourless (that is, oxides higher than nitric oxide are absent) led Lunge and Naef to suggest that a considerable part of the action here is the same as that which occurs in the de-nitrating portion of the Glover tower, namely,•



As the latter reaction becomes less intense, practically all the nitric oxide becomes converted into  $N_2O_3$ , and thus the colour of the gases in the succeeding chambers is increasingly reddish and completely dark-red in the last chamber.

A more recent review<sup>20</sup> of theories of the chamber reactions suggests the following as the most probable scheme :—





There is little doubt that the liquid phase plays a very important part in the process, and in fact Müller<sup>21</sup> has shown that the velocity of formation of sulphuric acid is directly dependent on the velocity of absorption of sulphur dioxide and oxides of nitrogen by the liquid phase. It will be noticed that the tendency in the modern systems described below is to carry out more and more of the reaction in the liquid phase.

The temperature of the first chamber is maintained at 60°–80°, and the gases are allowed to cool, until they leave the last chamber at about 40°, the maximum temperature for efficient working of the Gay-Lussac tower. The most rapid chemical action (probably mainly the de-nitrating action referred to above) takes place in the first half of the first chamber; in the second half, sulphuric acid production is comparatively small, but as the gases become remixed and the nitric oxide becomes more completely oxidised, the action revives in the second chamber and then declines, until at the exit from the last practically no sulphur dioxide remains unoxidised. Correct proportioning of the steam and the amount of oxides of nitrogen present is essential to efficient working of the chamber process; 98 per cent. of the sulphur originally admitted to the system should be converted into sulphuric acid. The process is controlled by frequent analyses of the exit gases from the Gay-Lussac tower, of the inlet gases to the Glover tower and of the chamber acid, nitrous vitriol, and finished Glover acid produced.

The above description of the chambers is intended to indicate the old mode of operation in which the pro-

cess was supposed to be mainly one of homogeneous gaseous catalysis. Many improvements have been made within the last few decades in order to economise the chamber space; the first of these consisted of the injection of water spray instead of steam into the chambers, when it was found that higher and narrower units could be employed with considerable saving of ground space. Obviously this is equivalent to carrying out more of the reaction in the liquid phase and less in the purely gaseous system.

At about the time that the German sulphuric-acid contact processes were coming into large-scale operation, efforts were made, and have been continued, further to reduce the chamber space. Meyer<sup>22</sup> introduced a system of circular chambers into which the gases were introduced tangentially, in order to induce flow in a spiral direction with consequent intimate mixing. Two very important further modifications out of a number of alternative propositions may also be mentioned:—

*The Mills-Packard System.*<sup>23</sup>—This consists of circular towers, narrower at the top than at the base, cooled externally by cold water, and fed from the top with a water spray. The towers are usually about 40 ft. high and 15–20 ft. in diameter. This system, in addition to economy in space occupied and in the amount of material (and therefore cost) of the installation, is claimed to tend to more regular and efficient progress of the reactions, and has come into extended use both in this country and America. Plant capable of producing over one million tons of sulphuric acid per annum has been erected throughout the world under the Mills-Packard patents.

*The Opl Tower.*<sup>24</sup>—This system consists of a series of towers, usually six in number, constructed on the lines of a fractionating column, the trays, of course, being made of lead or other acid-resisting material. The hot burner gases pass into the base of the first tower and from its top to the base of the second, and

so on through the whole set of towers in series. The first tower is fed with acid from the second tower, whilst in addition to acid from the succeeding towers water is added to the second, third and fourth, and additional nitric acid is also admitted to the second tower. This procedure again effects great economy in construction and space over the older form of chamber process, and has been increasingly used in the past twenty years on the Continent and also to some extent in England.

Many other intensive systems have been introduced in recent years. The Gaillard-Parrish plant<sup>25</sup> includes a high cylindrical tower fitted at the top with a "turbo-disperser" which injects dilute acid mist and maintains the contents in a state of turbulence. The intensification of the reaction is produced partly by the cooling of the walls by acid spray, and partly by causing more of the reaction to take place in the liquid phase. Although the process is not so well known in this country as abroad, one plant has been in successful operation here for several years. Other devices consist of arrangements by which pools of acid are formed in the chambers or towers through which air is injected (Hurt),<sup>27</sup> or devices for injecting the acid from the later chambers or towers in the form of a mist or spray into the first chamber or tower in order to ensure more efficient contact between the burner gases and the liquid acid spray.<sup>26</sup>

Obviously, bearing in mind the corrosive nature and density of the liquids to be handled in the course of the chamber process, the cost of construction and maintenance of the mechanical devices (acid pumps, elevators, etc.) necessary in these more intensive processes is a factor which has to be placed against the increase in efficiency which is obtained; for example, the use of an acid-spraying device is probably generally more economical than the practice of injecting air through pools of the liquid acid on account of lower power consumption. It will thus be seen that the

engineering and production costs of a modern chamber plant provide many complicated problems, but at the same time there is little doubt that the chamber process would hardly have held its own against the contact process had not the more intensive methods of working been brought into operation.

The Moritz Chemical Engineering Co. have developed a chamber plant<sup>28</sup> which, whilst embodying no mechanical intensifying arrangements, is claimed to be cheaper than and as efficient as the numerous intensive plants. The advantages are said to be due to the use of a series of tall rectangular chambers, in which the ratio of wall surface to volume is practically unity, communicating near the bottom through narrow passages wherein acid and gases pass in opposing directions. Brick ducts are provided in these passages to divide up the gas stream, and in the chambers to cause gas to ascend at the centre and descend near the walls.

A Moritz plant has been erected recently in this country at King's Lynn for the West Norfolk Farmers' Manure and Chemical Co-operative Company to supply acid for the manufacture of super-phosphate.<sup>29</sup> Sulphurous gases from eight pyrites burners with a total capacity of 40 tons pyrites/24 hours, are passed through Moritz electrostatic precipitators operating at 60,000 volts, and 96-98 per cent. of the dust is removed. The gases at 525°-550° enter the Glover tower, which is of Moritz design, 40 ft. high, 17 ft. in diameter and filled with acid-resisting bricks supported on lava grates. The gases then pass through seven Moritz chambers, 9 ft. long, 37 ft. 6 in. wide and 66 ft. high, fitted with the patented low communications. The gases from the last chamber pass through two Gay-Lussac towers 55 ft. high and 7 ft. by 16 ft. 6 in. in cross-section. These are filled with semi-permeable partitions which force the gas to traverse a devious path against the downcoming stream of acid. Catalytic oxidation of ammonia provides the nitrous gases

which enter the stream of sulphurous gases through a damper, either before the Glover tower, or between the latter and the first chamber. The space occupied by the towers and chambers in plan is stated to be only 135 ft. by 47 ft., and the entire plant can be controlled by one operator.

Some idea of the relation between chamber space and the weight of acid produced by the various methods which have been referred to may be gathered from the following table :—

	Cubic Feet Space (per lb. sulphur burnt per day).	Consumption of Nitrogen Oxides (as lb. nitre per 100 lb. sulphur).
Old . . .	16-20	2.5-4
Intensive . .	10	1.8-2.7
Mills-Packard	3	1.8-2.0
Opl . . .	2	2.2

*Purification and Concentration of Chamber Acid.*—

The acid coming direct from the chambers is liable to contain various impurities, including traces of lead, iron, arsenic, selenium, and also nitro-sulphonic acid. The Glover acid (commercial or brown oil of vitriol, B.O.V., 78 per cent.  $\text{H}_2\text{SO}_4$ ,  $140^\circ\text{Tw.}$ ,  $60^\circ\text{Baumé}$ ), will contain a still higher percentage of these impurities, including up to 1 per cent. of arsenic, both owing to the fact that concentration has taken place, and also to the removal of impurities from the burner gases with which it is made. Nevertheless this quality of acid is that which is mainly employed for most purposes where special purity is not necessary.

In many other cases, however, it is essential at least to ensure that elements such as arsenic, antimony, lead and selenium are completely absent. This can be effected by passing a current of hydrogen sulphide through the chamber acid, when arsenic, antimony and lead are wholly removed as insoluble sulphides,

and any selenium present is reduced to the elemental condition; higher oxides of nitrogen are converted at the same time into nitric oxide, which passes away with the excess of hydrogen sulphide. The hydrogen sulphide treatment is carried out either in lead-lined scrubbing towers or in mechanical washers; the treated acid is settled and finally filtered through porous earthenware material of the Filtros type.

To convert the Glover acid or brown oil of vitriol into commercial concentrated sulphuric acid ( $168^{\circ}$  Tw. or  $66^{\circ}$  Baumé), containing 96–98 per cent.  $\text{H}_2\text{SO}_4$ , a further process of concentration is required. This was formerly carried out in fire-heated acid-resisting pans of various types, or by passage of hot gases over the surface of Glover acid contained in shallow troughs, followed by scrubbing the gases through coke towers to remove acid fumes carried forward; this process is still used in some of the smaller works.

The most efficient modern method, however, is that due to Gaillard,<sup>30</sup> who, in 1906, designed what has come to be known as the Gaillard tower. This consists of a tall tower, about 60 ft. high and 6 ft. in diameter, constructed of masonry, somewhat narrower at the top than at the base, lined with acid-resisting bricks or Volvic lava, and fitted at the top with three atomising jets (Körting jets). The tower is not packed and is fed at the base with flue gases (from a coke-producer furnace) from which the dust has been settled, and which are at a temperature of about  $1,000^{\circ}$ . Gases pass up the tower and meet the acid, which descends in a fine spray, after being injected through the Körting nozzles at the top. Concentration of the acid to 96 per cent.  $\text{H}_2\text{SO}_4$  is readily effected, and the finished acid passes *via* a lead settling tank into a tank supplied with a lead cooling coil. The hot gases from the top of the tower are led to a recuperator consisting of a small lead tower fed with a spray of the original weak acid. This acid, which may form half of the total quantity passing through the main tower, is then admitted to

the latter. The gases enter the recuperator at about  $200^{\circ}$  and leave at  $100^{\circ}$ – $150^{\circ}$ , the heat given up being thus utilised to effect some preliminary warming of the acid entering the main tower. A tower of the dimensions given will produce about 40 tons of concentrated acid per day with a consumption of about 3–4 tons of coke. There is a loss of about 3–4 per cent. due mainly to sulphur trioxide carried away by the exit gases after recuperation, but experience in England during the war of 1914–1918 showed that this could be dealt with effectively by passage of the spent producer gases through a Cottrell electrostatic precipitation plant.

Another modern method which must be mentioned is the cascade process, in which a number of acid-resisting basins are arranged on a series of descending steps constructed in acid-resisting masonry, and heated by means of flues. Hot acid is supplied to the topmost basin and flows in succession down the series, meeting throughout a current of hot air which is passed upwards in the contrary direction. The final concentrated acid is passed through a lead cooler, settled and stored. Cascade plants are very largely used in the production of the commercial concentrated acid, but the loss as acid fumes is considerably greater than in the Gaillard tower, and may reach 15–20 per cent. Most of this, of course, can be recovered by passage of the exit air from the cascade system through a series of coke scrubbers fed, for example, with chamber acid. The material used for the dishes must be selected with care; various acid-resisting alloys are available at the present day and, in addition, vessels constructed of fused silica are also largely employed.

### References to Section II., Chapter VII

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## CHAPTER VIII

### CHLORINE MANUFACTURE BY THE DEACON OR WELDON PROCESSES

THIS chapter is mainly historical, for in it will be described some catalytic processes at one time indispensable for the manufacture of chlorine, but now either fallen into disuse entirely, or definitely on the decline, owing to various factors having combined to make electrolysis the more efficient method. It is true that the processes in question, devised some sixty years ago, were worked out more empirically and, perhaps, by rule-of-thumb methods, than technical catalytic actions of the present day, but they were nevertheless built up by means of sound experimental work, chiefly by chemists associated with one or other of the Lancashire alkali firms which later became the United Alkali Co., who brought them to a high standard of general efficiency.

The factors which have caused the gradual change from catalytic to electrolytic methods are somewhat as follows: At the time that the Deacon-Hurter and Weldon processes were first conceived, the Leblanc salt-cake process was in full operation, and its by-product, hydrochloric acid, was produced in large quantities, for which outlets were sought in various directions. One of these was in the conversion of the acid to bleaching liquor or powder, that is to say, a solution of sodium hypochlorite, or the solid bleaching powder,  $\text{CaCl}(\text{OCl})$ , formed by absorption of chlorine in lime. At that time this was practically the only form in which chlorine was employed on any scale; outside the laboratory there were no uses for chlorine gas, and liquid chlorine was a scientific curiosity. The fact that chlorine produced in the Deacon-Hurter or Weldon-

Péchiney processes was a dilute mixture of the gas with atmospheric nitrogen, etc., was not a serious hindrance to its absorption by lime, but at the present time far more chlorine is employed in the elementary form than as bleaching powder or liquor, and consequently the production of a diluted form of chlorine gas is far less advantageous than the manufacture of practically pure chlorine in bulk.

The recent uses for chlorine, to which reference is made, include its use in the indigo synthesis wherein aniline is condensed with chloracetic acid to produce phenylglycine, and chlorine is required for the chlorination of acetic acid. Still more recent uses which consume very large quantities of liquid chlorine are modern methods of petroleum refining and the chlorination or sterilisation of water supplies.

The ease with which liquid chlorine or compressed chlorine can now be produced is again connected with general developments in the alkali industry; for, just as the Leblanc process was largely displaced by the Solvay ammonia soda process, so, in turn, this is meeting with increasing competition from electrolytic methods. Even in this country, where electric power is relatively dear, brine solutions can be economically electrolysed in appropriate cells, so as to produce either caustic soda solution or, by the Hargreaves-Bird or similar processes, to give sodium carbonate solution. Chlorine is set free at the anode, in equivalent amount to the alkali obtained from the cathode compartment of the cell, and can be collected in a state of at least 97-98 per cent. purity. The evolved chlorine is carefully dried and compressed into steel cylinders or even into high-pressure tanks mounted on railway waggons. Owing to its relatively high boiling-point and critical temperature liquid chlorine does not present any special difficulty in transport, since its vapour pressure at ordinary temperatures is only of the order of 5-7 atmospheres.

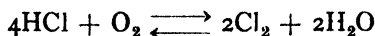
Whereas, for example, the maximum annual world's

production of bleaching powder by the Deacon-Hurter process has been estimated at 130,000 tons, equivalent to about 40,000 tons of chlorine, the present annual Continental production of chlorine from one type of cell (the Griesheim Elektron) is approximately 40,000 tons, whilst the annual total chlorine capacity of electrolytic plants in Canada and the United States is at present about 160,000 tons of chlorine, and correspondingly large quantities are produced annually by electrolysis in this country. These figures afford ample evidence of the way in which the older catalytic processes are being supplanted by electrolytic chlorine; it should also be stated that, although the existing Deacon-Hurter plants are still used for the production of bleaching powder, the latter is also made from electrolytic chlorine, and as the catalytic plants become worn out, they will doubtless in due course be entirely replaced by the electrolytic process.

In consequence of the moribund nature of the catalytic methods, we shall not deal with them in such detail as has been given to sulphuric acid, nitric acid, and ammonia; we will, however, give in a few words the main points of each of the three catalytic chlorine processes, taking them in decreasing order of efficiency but, as it happens, in the reverse of strict chronological order of their development.

#### The Deacon-Hurter Chlorine Process.

This method depends on the equilibrium reaction



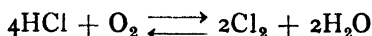
which was first employed on a technical scale by Deacon and Hurter<sup>1</sup> in 1868, and was improved in the succeeding years by these workers in England, and also by Hasenclever<sup>2</sup> in Germany, who introduced the use of purified dry hydrochloric acid in the process about 1883. As already stated, the process, although carefully studied experimentally, was worked out (so far as modern catalytic theories are

concerned) on a purely empirical basis. It was found that several metallic chlorides, notably cuprous chloride, caused the oxidation of hydrochloric acid by oxygen, and that a maximum conversion of the acid to chlorine occurred at about  $500^{\circ}$ , higher temperatures tending to reduce the yield; the working yield of chlorine obtained in practice, using dry hydrogen chloride, is about 65–70 per cent. Deacon and Hurter took the hydrochloric-acid gas from the salt-cake furnace, mixed it with four times its volume of air and passed it through iron superheaters into iron cylindrical chambers about 12 ft. wide, filled with small pieces of broken brick impregnated with cuprous chloride (the copper content of the catalyst being 0.6–0.7 per cent.); the catalyst vessels were maintained at  $450^{\circ}$ – $500^{\circ}$ . The exit gases from the catalyst chambers were passed through earthenware condensers to remove water and unchanged hydrochloric acid, after which the gases were led directly into the bleaching powder chambers. In this simple form of plant the yields varied considerably, and the catalyst rapidly lost its activity. The reason for the latter was found to be partly the volatility of cuprous chloride at the temperature of the reaction and partly the poisoning effect due to oxides of arsenic, sulphur and carbon, and other materials introduced with the gases. Drying the hydrochloric acid gas was found to induce a marked effect on the yield, whilst operation at a somewhat lower temperature ( $450^{\circ}$ ) reduced the volatilisation loss of the catalyst.

Thus the later forms of Deacon plant<sup>3</sup> consisted of a system of water scrubbers by which the crude hydrochloric acid was obtained in the form of solution. A current of air was blown through the crude acid and carried the vapour into the base of a tower filled with coke and fed at the top with concentrated sulphuric acid; a pure dry mixture of hydrochloric acid and air was then obtained, which was fed to the catalyst chamber. The batch of catalyst under these

conditions would normally have a life of about three months, at the end of which time volatilisation losses caused the chlorine production to fall below an efficient point; the loss of copper in this way amounted to about 3-4 pounds per ton of bleaching powder made.

At a much later date the equilibria at different temperatures in the action



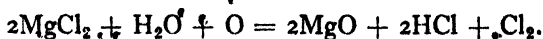
were studied by G. N. Lewis,<sup>4</sup> Falckenstein<sup>5</sup> and others, the results obtained confirming the technical practice, in that it was found that the percentage of chlorine at equilibrium diminished with rise of temperature and fell off very seriously above about 600°. At 430°-450°, the lowest temperature at which the cuprous chloride catalyst is reasonably active, the theoretical yield is of the order of 80 per cent. of hydrochloric acid converted to chlorine. Hurter and Deacon concluded from their investigations that the mechanism of the catalytic process depended on the production of an oxychloride as follows:—

- (1)  $\text{Cu}_2\text{Cl}_2 + \text{O}_2 = \text{CuO} \cdot \text{CuCl}_2$ .
- (2)  $\text{CuO} \cdot \text{CuCl}_2 + 2\text{HCl} = 2\text{CuCl}_2 + \text{H}_2\text{O}$
- (3)  $2\text{CuCl}_2 = \text{Cu}_2\text{Cl}_2 + \text{Cl}_2$ .

Subsequent work has confirmed these views and has also indicated that oxychlorides of other metals frequently give rise to the same series of reactions. Copper chloride, however, is the only one which has been found to give a useful yield of chlorine, that is, to promote the establishment of equilibrium sufficiently rapidly at a temperature low enough to permit of a reasonably high percentage of chlorine at equilibrium.

#### The Weldon-Péchiney Process.<sup>6</sup>

This process utilises an action somewhat similar to the Deacon-Hurter method:—



It was evolved by Weldon owing to the high losses

of chlorine in the original Weldon process, which is described below; although now defunct, it was worked in England, France and Germany to some extent for a considerable period. It was obviously designed to compete against the Deacon-Hurter process and depends, so far as its mechanism is concerned, practically on the alternate production of magnesium oxychloride and magnesium chloride.

The process consisted in evaporating a solution of magnesium chloride with powdered magnesium oxide in proportions to give the oxychloride  $\text{MgO.MgCl}_2$ . The solid oxychloride was powdered, dried at  $300^\circ$  and then passed into brick furnaces maintained at about  $1,000^\circ$ , in which it met a current of hot air. The above reaction then occurred, the mixture of chlorine, hydrogen chloride and residual air being separated as in the Deacon-Hurter process, and the hydrochloric acid employed in the production of fresh magnesium chloride.

#### The Weldon Process.<sup>7</sup>

This method came into use almost at the same time as the original Deacon-Hurter process and consisted substantially of the following series of reactions:—

- (1)  $\text{MnO}_2 + 4\text{HCl} = \text{MnCl}_2 + \text{Cl}_2 + 2\text{H}_2\text{O}$ .
- (2)  $\text{MnCl}_2 + \text{Ca(OH)}_2 = \text{Mn(OH)}_2 + \text{CaCl}_2$ .
- (3)  $2\text{Mn(OH)}_2 + \text{O}_2 + \text{Ca(OH)}_2 = \text{CaO.2MnO}_2 + 3\text{H}_2\text{O}$ .
- (4)  $2\text{CaO.MnO}_2 + 2\text{Ca(OH)}_2 + \text{MnCl}_2 + \text{O}_2 = 2(\text{CaO.2MnO}_2 + 2\text{CaCl}_2 + 2\text{H}_2\text{O})$ .
- (5)  $\text{CaO.2MnO}_2 + 2\text{HCl} = 2\text{MnO}_2 + \text{CaCl}_2 + \text{H}_2\text{O}$ .

The "catalyst" in this process may therefore be looked upon as oxides of manganese in varying stages of oxidation. The drawback of the process is that in the course of reconversion of the manganous salt to manganese dioxide, considerable quantities of chlorine are wasted in the production of the by-product calcium chloride, nearly 60 per cent. of the original hydrochloric acid being ultimately trans-

formed into calcium chloride. Nevertheless, for a certain period, the process was able to compete fairly successfully with the Deacon-Hurter process, because in addition to producing chlorine it served to convert the natural mineral manganese dioxide or pyrolusite into the finely precipitated form known as Weldon mud, which was a much more useful and reactive form of the dioxide for service in the further manufacture of permanganates, manganates and similar oxidised manganese compounds. Commencing with the natural manganese dioxide ore, this was heated in special stoneware stills with concentrated hydrochloric acid, and the chlorine initially evolved away or finally blown out with air for production of bleaching powder. The acid solution of manganous chloride in the stills was neutralised with natural chalk and settled in tanks, after which the neutral salt solution was pumped into an elevated storage tank from which it was charged into an oxidiser, which consisted of a tall vertical vessel kept at about  $55^{\circ}$ – $60^{\circ}$  with a current of live steam. In this vessel sufficient milk of lime was added to precipitate all the manganese as manganous hydroxide and to give, in addition, a 30–40 per cent. excess of lime. The presence of this excess of lime is essential for the ensuing oxidation, since the manganous hydroxide is not quantitatively converted to manganese dioxide in presence of air, except under alkaline conditions (that is, so that calcium manganite is formed). The oxidation of the alkaline liquor was effected by blowing a current of air through the tank, when the action (3) took place. A further charge of liquor was then added and the second oxidation (4) carried out, thus producing a combination in which twice as much manganese dioxide was combined with the lime as in the first stage. The finished suspension was then passed to settling tanks and the Weldon mud recovered either for further oxidation to manganates, etc., or for neutralisation and re-use in the chlorine process.





## CHAPTER IX

### REMOVAL OF HYDROGEN SULPHIDE AND ORGANIC SULPHUR COMPOUNDS FROM GASES

IN addition to the important industries discussed in preceding chapters, such as the manufacture of ammonia, nitric acid, sulphuric acid or hydrogen, there are a number of other technical processes wherein molecules in the gaseous phase interact at the surface of metals or of metallic oxides. Before dealing (in Chapter X) with some important catalytic processes of this nature employed in the manufacture of certain organic chemicals, we shall consider in the present chapter those methods which have been applied to the removal of sulphur compounds from town's-gas or other hydrocarbon gases.

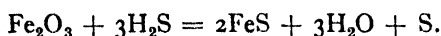
When coal is carbonised, gaseous sulphur compounds are always produced, emanating principally from pyrites or other inorganic sulphide present in the original coal. Hydrogen sulphide is the chief constituent of these gaseous sulphur compounds, but there are also present organic sulphur compounds, chiefly carbon disulphide, carbon oxysulphide and a certain proportion of organic sulphides and mercaptans (thiols).

#### Purification of Town's Gas from Hydrogen Sulphide.

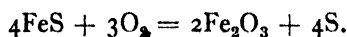
Crude coal-gas, after removal of tar, ammonia, etc., in the scrubbing plant, will contain relatively large amounts (*e.g.*, 0.5–1.5 per cent.) of free hydrogen sulphide, whereas the permissible amount of this material in the gas supplied to consumers is strictly limited by law. The removal of this impurity has therefore to be carried out thoroughly and rigorously.

Originally it was the usual custom to pass the

gas over lime purifiers, when calcium sulphide and carbonate were formed and hydrogen sulphide and carbon dioxide were removed. Compared with the modern process about to be described, the use of lime is costly, and the disposal of the residual spent lime sludge is difficult and somewhat of a nuisance. More modern practice consists in passing the gas over and through masses of porous iron oxide ore when, in presence of moisture, actions similar to the following take place :—



The gas is led through a series of very large cubical or rectangular steel "boxes," which contain a fairly porous form of natural ferric oxide, such as spathic iron ore or bog iron ore, or possibly masses of precipitated ferric hydroxide mixed with sawdust or other light solid in order to render the mass sufficiently permeable to comparatively free passage of the gas. The purification is conducted on the counter-current system, *i.e.*, the crude coal-gas passes first through a box containing nearly exhausted iron oxide and then progressively through the series until, in the final box, it meets with a comparatively fresh charge of the iron oxide. When the charge of ore in a box becomes so far spent that it ceases to absorb hydrogen sulphide efficiently, the iron sulphide is re-transformed by air into ferric oxide, with simultaneous production of free sulphur :—

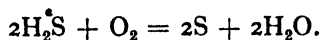


The re-oxidised ore, still containing liberated sulphur, can then be used again quite efficiently in the removal of hydrogen sulphide; and this cycle of operations can be carried on until the ore contains about 50 per cent. of free sulphur. The fully-spent ore then becomes a quite useful source of sulphur for the manufacture of sulphuric acid, and is by no means a useless waste product. Indeed a considerable amount of the material is, so to speak, hired out to

gas undertakings by chemical manufacturers, who eventually burn the deposited sulphur from the fully spent ore, thus using it as raw material in the manufacture of sulphuric acid.

Spent iron oxide has also sometimes been used as a fertiliser, particularly in France, but owing to the presence in it of toxic compounds, it must be applied to the soil well in advance of sowing-time.

It will be seen that this process is semi-catalytic in nature in so far that the iron oxide is used over and over again to carry out the same sequence of chemical changes. In recent gasworks practice it has been made more completely catalytic by carrying out the purification in presence of a small amount of added air. This came about first of all because it was observed that the working life of a given batch of iron oxide ore on the old system varied very considerably, and this was traced to differences in the crude gas (which always contains small but variable amounts of free oxygen). The greater the amount of oxygen in the crude gas, the longer was the efficiency of a purifier box maintained—due, of course, to the fact that both actions expressed in the above equations were proceeding concurrently, so that essentially the chemical action concerned became



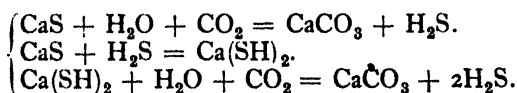
It has, therefore, become the practice to mix very small proportions of air with the crude gas and to pass the mixture through the iron-oxide purifiers, thus increasing the working period of a given batch of ore from a few days to many months; in fact, until the free sulphur content of the treated ore becomes sufficiently high to make it of economic value to the sulphuric acid manufacturer. The operation of this process demands careful chemical control, however, because the sequence of actions culminating in oxidation of hydrogen sulphide to free sulphur and water is accompanied by development of considerable heat,

and it is necessary so to arrange the proportion of oxygen present, and the velocity of passage of the gas through the purifiers, that no undue increase of temperature takes place.

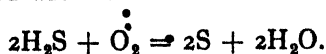
It has also been found that the use of crude ore is not the most efficient means of carrying out the catalytic action, and it is becoming more and more the custom to employ precipitated iron oxide as described above, or quite frequently, in modern practice, to supplement the use of iron oxide with that of precipitated manganese oxides; for example, Weldon mud derived from the catalytic production of chlorine by the Weldon process (*cf.* this Section, Chapter VIII, p. 229).

#### The Chance Sulphur-recovery Process.

In the well-known Chance process for recovering sulphur from the alkali waste (calcium sulphides) of the Leblanc soda-ash process, a current of carbon dioxide is passed through a series of scrubbing towers counter-current to a suspension of the alkali waste, whereby all the combined sulphur is removed as hydrogen sulphide :—



The effluent gas is collected, mixed with just sufficient air to provide a ratio of two volumes of hydrogen sulphide to one of oxygen and passed up into a converter known as a Claus kiln, which consists of a producer with a grating on which rests a mass of bog iron ore or similar material. Once combustion has been started locally oxidation proceeds exothermally at the surface of the iron oxide :—



The temperature requires careful regulation, otherwise undesired side reactions set in; the temperature

of the exit gases should not greatly exceed  $300^{\circ}$  in order to obtain the maximum yield of sulphur.

According to Rideal and Taylor the mechanism of the oxidation in the Claus kiln is the same as that in an ordinary iron oxide gas purifier in presence of small quantities of oxygen.

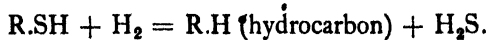
#### Removal of Organic Sulphur Compounds from Town's Gas.

The removal of the organic sulphur compounds is much more difficult than that of free hydrogen sulphide, and it is only within the last thirty years that really satisfactory processes to this end have been devised. The old system of removing hydrogen sulphide by lime also eliminated a certain proportion of combined organic sulphur compounds, but the process was not by any means complete.

The basis of modern procedure for almost complete elimination of combined sulphur from coal-gas rests upon the work of Vernon Harcourt,<sup>1</sup> who many years ago, in the course of his work as gas examiner, devised a laboratory method for the analytical determination of the total combined sulphur in coal-gas. This consisted in passing a defined volume of the gas through a heated tube or other receptacle containing pumice, which had been impregnated with a solution of platinum chloride and reduced. By this means all organic sulphur compounds were converted into free hydrogen sulphide, which was then estimated colorimetrically or otherwise. The action in the case of carbon disulphide, for example, may be represented as



whilst a mercaptan of the general formula  $\text{R.SH}$  would be attacked as follows :—



Harcourt, indeed, suggested that the analytical process might be modified for technical purposes by passing

the heated gas from the retorts through a mass of heated iron turnings or similar material, but nothing appears to have come of the suggestion. It is obvious, of course, that in dealing with a material such as coal-gas, the cost of treatment must be kept extraordinarily low, and a process which involved, for example, an extra cost of 1d. per thousand cubic feet would be regarded with considerable disfavour. The use of costly catalyst or plant, unless either of these are practically imperishable, is therefore out of the question.

There are, however, at least three systems which have been proposed for economic catalytic removal of organic sulphur compounds from coal-gas, and two of these have been in operation on a very large scale.

Nearly thirty years ago the South Metropolitan Gas Co. commenced investigations on the use of nickel for catalytic removal of sulphur, and in 1914 and 1915 Carpenter<sup>2</sup> and Evans<sup>3</sup> gave detailed accounts of the results which had then been obtained. The most suitable catalytic material for this particular purpose was found to be balls of fireclay which were impregnated with nickel chloride, dried and charged into the catalyst retorts. The process is carried out at 450°, and nickel produced at this temperature from the chloride by reduction in coal-gas causes the organic sulphur compounds to be decomposed in exactly the same way as in Harcourt's platinum process. The carbon produced is deposited over the catalyst, and in consequence the amount of action progressively declines; the plant has therefore to be so arranged that one or more catalyst units are periodically out of action whilst the deposited carbon is burned off by passage of hot air over the spent catalyst. This process effects sufficiently complete removal of the carbon to permit the nickel again to function efficiently in decomposition of the sulphur compounds.

Large-scale plants have been erected for the opera-

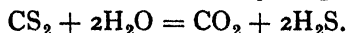
tion of this process, the economics of which were found to depend not so much on the original capital cost of the plant, or on the cost of the catalyst and its periodical recuperation, as upon the heat consumption necessary to raise the gas to the temperature of  $450^{\circ}$ , at which the reaction proceeds. This factor, however, was dealt with satisfactorily by means of an elaborate system of heat interchangers whereby the gas, after passage through the catalyst chamber, transfers its heat to untreated gas which is coming forward towards the catalyst. The average reduction of the sulphur content in the coal-gas is about 80 per cent., and the treated gas contains 6–8 grains of sulphur per 100 cubic feet, whilst its illuminating power is unimpaired; the average cost of the process is estimated at not more than 0.3d. per 1,000 cubic feet.

Somewhat prior to the work just recorded, a process<sup>4</sup> had been worked out in the United States on lines more nearly analogous to the original proposals of Vernon Harcourt. The plant proposed consisted of two superheaters filled with chequer work, as in a water-gas plant, with a gas-producer in between. Each superheater is employed alternately in the purification of coal-gas, which takes place at a much higher temperature than in the South Metropolitan process (*e.g.*, from  $700^{\circ}$ – $900^{\circ}$ ). This temperature is attained by burning producer-gas in that superheater which, at the moment, is not being used for coal-gas purification. Pre-heated coal-gas is then passed through it until the temperature declines below the lower limit mentioned, when the unit is again subjected to the heating process. In the meantime the second unit has been re-heated by producer-gas and is ready to deal with coal-gas. Carbon deposited on the reduced iron and ironwork of the unit is periodically removed by passage of a current of hot air. This process has been worked on an extensive scale and causes considerable reduction in the content of combined sulphur, the stated average reduction of the latter being about 70 per cent., and the



average cost of working being in the neighbourhood of  $\frac{1}{2}d.$  per 1,000 cubic feet.

Another process for the removal of organic sulphur compounds from coal-gas was proposed by Guillet <sup>5</sup> in 1912. This consisted in passing coal-gas over iron oxide instead of a metallic catalyst, at temperatures between  $130^{\circ}$  and  $300^{\circ}$ . Under these conditions carbon disulphide is decomposed in presence of moisture with formation of free hydrogen sulphide :—



The hydrogen sulphide formed is, of course, removed by the iron oxide and converted into ferrous sulphide, so that intermittent re-conversion of the latter back to the fully oxidised form is necessary. It seems possible, however, that the process might be so modified that continuous conversion of the hydrogen sulphide to free sulphur might be arrived at as in the analogous process for removal of hydrogen sulphide by iron oxide (p. 234) ; or, as Rideal and Taylor have suggested, since it is found that in the catalytic process for the manufacture of hydrogen from water-gas (*cf.* this Section, Chapter II, p. 87) all sulphur compounds are converted at  $500^{\circ}$  into hydrogen sulphide, these conditions may possibly be found practicable in a modified form of the Guillet process. Of course, other things being equal, purification at the lower temperatures suggested by Guillet would be less costly than a process operating at  $500^{\circ}$  (*cf.* also Section II, Chapter III, p. 116).

## CHAPTER 'X

### ACTION OF METALS OR METALLIC OXIDES ON ORGANIC COMPOUNDS IN THE GASEOUS (VAPOUR) STATE

MANY organic (carbon) compounds undergo chemical changes when, in the state of vapour or liquid, they come in contact with specific metals or metallic oxides which have been prepared in suitable form to display catalytic activity. The most familiar groups of such reactions are recalled by the classical work of Sabatier and his colleagues on hydrogenation and dehydrogenation of organic compounds in the gaseous state by certain metals, and on the respectively dehydrogenating or dehydrating actions exerted by different metallic oxides on the vapours of a number of alcohols. The many instances of organic compounds which undergo various catalytic transformations at solid metal or metallic oxide surfaces do not lend themselves very readily to systematic classification, even when, as at present, we are concerned only with processes which have proved to be, or seem likely to be, of industrial utility. As a commencement, we propose to deal in the present chapter with those cases in which a solid catalyst acts in contact with organic compounds in the state of *vapour*. To a large extent, also, it is possible to consider separately those processes in which (i.) metals, and (ii.) metallic oxides are the respective catalysts; but it is less easy to pursue a logical method of treatment as regards the kind of chemical action involved, which, in different cases, may be of the nature of hydrogenation, dehydrogenation, oxidation or dehydration.

This chapter is therefore prefaced with a brief outline of its contents, in order to indicate the topics which will be discussed. It will be seen that these

include a number of industrial processes of considerable importance to the organic chemical industry.

### (i.) *Metals as Catalysts*

Page.		Process.
241	Formaldehyde from methyl alcohol . . .	Oxidation.
245	Acetaldehyde from ethyl alcohol . . .	Dehydrogenation and oxidation.
249	Other aldehydes or ketones from alcohols . . .	Dehydrogenation.
250	Alcohols (ethyl, isopropyl, <i>n</i> -butyl) from aldehydes or ketones . . .	Hydrogenation.

### (ii.) *Metallic Oxides as Catalysts*

254	Olefines and ethers from alcohols . . .	Dehydration.
256	Ethylene from alcohol . . .	"
258	Ketones (acetone) from acids (acetic acid) . . .	"
260	Acetone from alcohol or acetylene . . .	Complex.
263	Oxidation of hydrocarbons . . .	Oxidation.
	(naphthalene → phthalic anhydride; toluene → benzaldehyde and benzoic acid; benzene → maleic acid; anthracene → anthraquinone, etc.).	

### (i.) METALS AS CATALYSTS

#### Production of Aldehydes and Ketones by Dehydrogenation of Alcohols.

Certain aldehydes and ketones, particularly the former, are of considerable technical value at the present day, but in a number of cases their production by the ordinary processes of oxidation, etc., is difficult to control, and good yields of the desired products are not always forthcoming. A very useful, if minor, application of catalysis is the passage of the vapour of a suitable alcohol over a metallic catalyst, usually either copper or nickel, when decomposition occurs, a molecule of hydrogen being liberated together with a molecule of an aldehyde (from a primary alcohol) or a ketone (from a secondary alcohol). The utility of this reaction may be gathered from discussion of the technical production of formaldehyde, acetaldehyde, butyric aldehyde and methylethylketone from the corresponding alcohols.

*Formaldehyde.*—The case of formaldehyde stands a

little apart from the others in so far that it has not yet been found feasible to produce this substance by simple dehydrogenation of methyl alcohol; dehydrogenation of methyl alcohol occurs extremely readily in presence of prepared copper at  $250^{\circ}$ – $300^{\circ}$  or of prepared nickel at a somewhat lower temperature, but the formaldehyde which is produced is further attacked and the yields obtained are only of a very small order. In this case, therefore, recourse is had to oxidation rather than simple dehydrogenation, and a mixture of methyl alcohol and air is passed over prepared copper or silver under carefully controlled conditions. Many processes for carrying out this reaction have been patented, but the fullest details of the process in its present form have been given by Orloff.<sup>1</sup>

The general operation of a formaldehyde plant of this kind may be described briefly as follows: The catalyst consists of fine metal gauze, either of platinum, silver, silver-copper alloy, or, most usually, of copper alone. Formaldehyde is an intermediate product in the oxidation of methyl alcohol, and it is obvious that, given sufficient oxygen, further transformation of the aldehyde to formic acid, or even to carbon dioxide and water, will take place equally readily, or more readily, than the desired oxidation. Consequently the temperature of the catalyst must be maintained within exceptionally narrow limits, and also the time of contact of the interacting gases with the catalyst must be cut down to the value which is found to lead to the highest yield of formaldehyde. The time of contact depends, of course, upon the rate of flow of the mixed gases and the length of the layer of catalyst to which they are exposed. In practice, the layer of catalyst employed is extremely short; for example, if rolls of 15-mesh copper gauze are used, the layer may be about 120 mm. in length, whereas, with finer gauze of 100 mesh, a length of 70 mm. is found to be better. In Orloff's apparatus the catalyst

chamber is built up of a very large number of copper tubes, set concentrically in two copper plates. Each tube is 80 cm. long and contains a closely-fitting glass tube, 30 cm. long and about 1.5 cm. diameter, in which is placed a 12 cm. length of closely-rolled copper gauze. The catalyst is heated up to the requisite temperature by preliminary ignition of the reacting gases by a sparking device, after which the temperature is maintained by the exothermal nature of the action, and is adjusted to the rate of flow of the mixed gases. A catalyst unit comprising six concentric rings of tubes as described (169 in all) will deal with about 17 kg. of methyl alcohol per hour and produce therefrom about 19 kg. of commercial formalin (40 per cent. formaldehyde).

The proportion of air to methyl alcohol and the rate of flow of the mixture have been studied exhaustively both by Orloff<sup>1</sup> and by Le Blanc and Plaschke,<sup>2</sup> and it appears that, with copper catalyst at 450°, the highest yield of formaldehyde results when one volume of methyl alcohol and 0.315 volumes of oxygen are present, whilst the highest conversion of methyl alcohol to oxidised products requires 0.39 volumes of oxygen for one volume of methyl alcohol. It will be seen, therefore, that either a formalin solution will be obtained containing some unchanged methyl alcohol or the yield of formaldehyde will suffer if complete oxidation of the methyl alcohol is secured. The process is generally carried out so that the highest yield rather than the highest conversion is obtained, and, so far as possible, unchanged methyl alcohol is recovered from the products of oxidation by passage of the latter through a fractionating column.

In operating the formaldehyde plant, methyl alcohol (which should be as free as possible from acetone and water) is fed into a small tank in which it is warmed to about 40° or 50° by means of a closed coil; a current of compressed air is injected into the warmed methyl alcohol at such a rate that the catalyst chamber is

maintained steadily at  $450^{\circ}$  by the heat of oxidation. By adjustment of the temperature of the methyl alcohol in the tank, the proportions of methyl alcohol and air passing on to the catalyst chamber are maintained so that there are 0.32 volumes of oxygen present for every volume of methyl alcohol vapour. The methyl alcohol-air mixture passes from the mixing tank directly into the catalyst chamber, where the greater part of the methyl alcohol is converted to formaldehyde with a minimum of more intensive oxidation. The exit gases from the catalyst pass into the lower part of a plate fractionating column, when an aqueous solution of formaldehyde separates and is run off from the base of the column (the water having been produced concurrently in the oxidation). Unchanged methyl alcohol vapour, a little formaldehyde, and any carbon dioxide pass through the column, and the methyl alcohol is subsequently condensed and returned to the process. The aqueous formaldehyde solution separated at the base of the main fractionating column constitutes commercial "formalin," and should contain 38-40 per cent. of formaldehyde with not more than 10-12 per cent. of methyl alcohol.

A recent patent <sup>3</sup> of the I.G. Farbenindustrie A.-G. claims the production of 60 per cent. formalin solution by a similar process of oxidation in which completely anhydrous methyl alcohol is employed. The heat of the reaction products may be used to preheat the constituents of the reaction mixture (methyl alcohol and air) separately, the latter then being mixed at a temperature below that of the reaction chamber (I.G. Farbenindustrie <sup>4</sup>); or the air for the oxidation may be first led through an inner tube in the catalyst chamber and, thus preheated, mixed with methyl alcohol vapour and passed into the catalyst chamber itself (Barbet <sup>5</sup>).

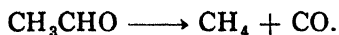
Natta,<sup>6</sup> in a review of factors determining the yield of formaldehyde, discussed the practical difficulties of simple dehydrogenation of methyl alcohol in absence

of air. The decomposition of the formaldehyde so produced can be partly overcome by the presence in large concentrations of carbon monoxide or dioxide, but this is not a practical solution. Natta and Strada found, however, that in presence of a large excess of carbon dioxide (that formed as a by-product (*cf.* pp. 86, 107) in the manufacture of hydrogen or methyl alcohol can be utilised) and a certain amount of air (10–20 per cent. of that necessary for complete oxidation of the methyl alcohol), a combined oxidation and dehydrogenation of the methyl alcohol can be effected. The heat required by the endothermic dehydrogenation is supplied by that of the exothermic oxidation reaction, and 94–96 per cent. yields of formaldehyde are stated to be possible when oxidation and dehydrogenation of methyl alcohol are thus carried on simultaneously in a protective atmosphere of carbon dioxide.

Ordinary 40 per cent. formalin is manufactured on a fairly considerable scale, and is used on the one hand as an important antiseptic and disinfectant and on the other in commercial synthetic organic chemistry, especially in the production of certain dyestuffs (for example, of the acridine series) and also of a number of fine chemicals, the most familiar of which is probably hexamethylenetetramine or "hexamine," a condensation product of six molecules of formaldehyde with four molecules of ammonia. It is also required in quantity for the manufacture of synthetic resins by its condensation with phenols (Bakelite, p. 424) or urea.

*Dehydrogenation of Ethyl Alcohol and Higher Alcohols in presence of Metallic Copper.*—The remaining lower alcohols of the ordinary aliphatic series are readily converted into corresponding aldehydes or ketones by passage over reduced copper<sup>7</sup> at about 300°, a process which has been employed technically for the preparation of several aldehydes and ketones of commercial interest. Nickel is more active than copper as a dehydrogenating catalyst, but it has the

disadvantage that it exercises further action on the carbonylic derivatives formed and tends to produce carbon monoxide and saturated hydrocarbons; for example,

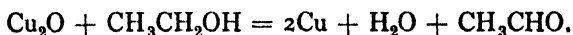


Copper, at the temperature indicated, does not give rise to this complication, and moreover it can be prepared conveniently in a form which permits of periodical recuperation by simple oxidation in a current of hot air. The production of copper in this form has been described by Legg and Adam<sup>8</sup> and consists in the manufacture of fused cuprous oxide, either by melting down ordinary black copper oxide or by burning copper turnings in a current of air heated to about 1,200°. The solidified cuprous oxide forms a hard brittle crystalline mass of a bluish-black colour, which can easily be broken down into granules of any desired size, for example  $\frac{1}{4}$ – $\frac{3}{8}$  in. mesh. This oxide has the great advantage of being reducible at a low temperature (220°–300°), and of retaining its external size after reduction, although the density of the metallic copper produced is considerably higher than that of the oxide. In other words, a very porous mass of spongy copper is obtained which is of considerable catalytic activity; the combination of porosity and hard granular structure renders it particularly suitable for use as a vapour catalyst.

In producing an aldehyde or ketone by means of this catalyst, the appropriate alcohol is first of all volatilised from a still and the vapour passed through a series of heated copper tubes in order to bring it to a temperature of 300°, or somewhat higher, the conversion of an alcohol to an aldehyde or ketone being an endothermic action. The pre-heated vapours then pass into a tubular retort (or retorts) packed with the cuprous oxide prepared as described. If the alcohol employed is of low molecular weight, for example, ethyl alcohol or isopropyl alcohol, the cuprous oxide is reducible by the alcohol at 280°–300°, and



it is unnecessary to carry out a preliminary reduction in hydrogen (a procedure which may be necessary in the case of certain of the higher alcohols); with ethyl alcohol, the cuprous oxide is reduced almost quantitatively according to the equation



The dehydrogenation process is usually incomplete at  $300^\circ$ , but if higher temperatures are employed side reactions complicate matters to a considerable extent; for example, at  $350^\circ$  or higher, ethyl alcohol yields not only acetaldehyde, but increasing amounts of carbon dioxide, carbon monoxide and saturated and olefinic gaseous hydrocarbons, in addition to products of polymerisation of the aldehyde, which are deposited on the catalyst and hinder the process. It is therefore desirable to conduct the operation at the lower temperature and obtain a maximum yield of aldehyde or ketone rather than the maximum decomposition of the alcohol present. The vapours emerging from the catalyst chamber thus consist of a mixture of aldehyde (or ketone) with unchanged alcohol, hydrogen in equimolecular proportion to the aldehyde (or ketone) produced, and 1 or 2 per cent. of oxides of carbon and gaseous hydrocarbons.

In more recent practice it is usual (as in the case of formaldehyde from methyl alcohol, p. 242) to carry out the dehydrogenation of the alcohol in presence of a certain proportion of air, dehydrogenation and direct oxidation then proceeding concurrently. The heat evolved by the oxidation is absorbed in maintaining the endothermal dehydrogenation reaction, with the result that a constant temperature can be maintained (without external heating) at which dehydrogenation proceeds steadily, whilst the aldehyde produced by oxidation is not further decomposed. By this means the conversion of alcohol to aldehyde at each passage over the catalyst is greatly increased (*e.g.*, to 75–85 per cent.) with no loss in yield and considerable economy

of heat in the subsequent fractionation of the products.

In either form of the process, the gases coming away from the catalyst are conveniently passed through a heat interchanger and then into a fractionating column heated by live steam and constructed in two sections, in the first of which the unchanged alcohol is separated from aldehyde (or ketone) and hydrogen, condensed and returned to the process. The lighter constituents of the mixture pass through to the second column, where the last traces of alcohol are eliminated and returned to the first column, whilst the aldehyde or ketone is condensed continuously at the top of the second column; hydrogen and permanent gases pass on through a water scrubber in which the last traces of aldehyde or ketone are separated. The operation of such a column is similar in general principle to that of the ether-alcohol column, which is described in some detail in Section IV, Chapter III, p. 416.

These processes have been employed technically in the following cases :—

*Acetaldehyde*.—The optimum yield of acetaldehyde is obtained at temperatures not exceeding  $300^{\circ}$ , when about 20–25 per cent. of the alcohol present is converted into acetaldehyde at each passage over the catalyst; the remainder is recovered by fractionation, as described, and at the same time acetaldehyde of a high degree of purity is withdrawn from the top of the column. The overall yield of acetaldehyde from ethyl alcohol by this process is about 90–92 per cent. Minor amounts of ethyl acetate and other condensation products of acetaldehyde are produced in addition to a small percentage of permanent gases, and the catalyst slowly declines in activity owing to deposition of a layer of complex condensation products. After twenty-four to forty-eight hours' use it is expedient to interrupt the process and reoxidise the copper superficially in a current of hot air when, on subsequent reduction at or below  $300^{\circ}$ , its activity is fully restored.

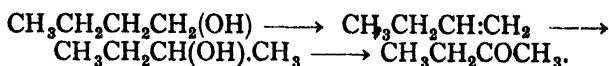
By means of the combined dehydrogenation and oxidation process already mentioned on p. 247, industrial alcohol is now converted in this country into acetaldehyde at a price which can compete successfully with that of the aldehyde produced by hydration of acetylene (Section IV, Chapter I, p. 368). For example, the vapour from 95 per cent. alcohol is passed with 35–75 per cent. of the oxygen necessary for oxidation, with or without steam, over silver gauze at  $450^{\circ}$ – $550^{\circ}$ .<sup>9</sup> Heat exchange is used in preheating the gases before passage over the catalyst. With an alcohol-air ratio of 1 : 1.1 by volume, 20 per cent. of the aldehyde produced is formed by dehydrogenation and the exit gases contain 10 per cent. of hydrogen. Another patent<sup>10</sup> describes apparatus in which a mixture of alcohol, steam and air in predetermined proportions is passed over copper at  $420^{\circ}$ – $440^{\circ}$  or silver at  $450^{\circ}$ – $500^{\circ}$ , the reaction proceeding without extraneous supply of heat and the temperature being controlled by the proportion of steam admitted to the mixture. Mixed copper-silver catalysts have also been proposed for the process.

(For direct conversion of ethyl alcohol to ethyl acetate or butyl and higher alcohols in presence of copper catalysts see Section IV., Chapter I, p. 379.)

Propyl alcohol and isopropyl alcohol are equally readily dehydrogenated, respectively, to propionic aldehyde and acetone, but this is of theoretical rather than of technical interest. On the other hand, *normal butyl aldehyde* has been produced from normal butyl alcohol<sup>11</sup> by the copper process, the conversion to aldehyde at  $300^{\circ}$ – $320^{\circ}$  being in this case of the order of 80–90 per cent.

It has also been suggested<sup>12</sup> to manufacture *methylethylketone* by similar dehydrogenation of methylethylcarbinol (isobutyl alcohol), the conversion again being relatively large in presence of copper at  $300^{\circ}$ . It should be pointed out that by a sequence of catalytic processes it is possible to pass from normal

butyl alcohol to methylethylketone in the following three stages :—



Certain hydro-aromatic alcohols also lend themselves to this reaction ; for example, cyclo-hexanol<sup>13</sup> and the methyl cyclo-hexanols (produced from phenol or the cresols by hydrogenation, *cf* p. 296) are rapidly converted into the corresponding cyclo-hexanone or methyl cyclo-hexanones in presence of copper at 300°. The same process can also be applied to borneol,<sup>14</sup> from which camphor is obtained in good yield on dehydrogenation.

#### Production of Alcohols by Hydrogenation of Aldehydes or Ketones.

This action is the reverse of that with which we have just dealt, and may prove to be of technical utility in a number of cases. The same metals as those employed in dehydrogenation are effective for reduction of aldehydes or ketones,<sup>15</sup> but the change takes place at a lower temperature and, in general, it is found that nickel is a more efficient catalyst in this case than copper. The nickel catalyst may be employed on a porous support (for example, pumice impregnated with the nickel salt and reduced), or in the form of activated nickel turnings of the type devised by Bolton and Lush<sup>16</sup> (*cf* p. 283). Certain high-boiling ketones or aldehydes are hydrogenated to the corresponding alcohols in the liquid state (a subject which is dealt with in Chapter XI of this Section, p. 301), and the only cases of production of alcohols by hydrogenation in the vapour phase, which we need mention specifically are those of ethyl alcohol and isopropyl alcohol.

*Ethyl Alcohol.*—The production of ethyl alcohol from acetaldehyde has been shown to be technically prac-

ticable on a large scale in Switzerland,<sup>17</sup> but at present the cost of alcohol derived in this way from acetylene does not compete under the most favourable conditions with that of fermentation alcohol. In view of the wide number of other technically valuable products which can be obtained from acetaldehyde it is doubtful whether, even if supplies of fermentation alcohol failed, this method of preparation would compete with, for example, the recovery of alcohol from waste gases containing ethylene (*cf.* Section IV, Chapter I, p. 387).

The hydrogenation of acetaldehyde has been carried out in Switzerland in presence of nickel deposited on pumice as employed by Sabatier,<sup>15</sup> and undoubtedly the above-mentioned Bolton and Lush<sup>16</sup> catalyst would serve the purpose even better. The layout of an aldehyde reduction plant is similar to that employed in other vapour catalyses with the exception that, in this instance, it is more necessary to secure rapid and adequate removal of the heat of reaction than to preheat the interacting gases to the required temperature. Any increase of temperature beyond about 150° causes considerable destruction of acetaldehyde in presence of nickel, and therefore the temperature of the system must be kept definitely below this point, whilst it is also found best to conduct the process in presence of a very large excess of hydrogen.<sup>18</sup> The Elektrizitätswerk Lonza<sup>17</sup> also recommends that the hydrogen should contain 0.3 per cent. of oxygen, as this tends to restrain the production of ethyl ether as a by-product. On a large scale, overall yields of 90 per cent. of ethyl alcohol from acetaldehyde have been consistently obtained by this process.

It has been estimated that, assuming yields of 80, 90 and 90 per cent. in the three stages, carbide to acetylene, acetylene to aldehyde, aldehyde to alcohol, one ton of alcohol should result from two tons of crude carbide, and that the total cost of one ton of alcohol might not exceed the following :—

	£
Carbide (2 tons at £8 per ton) . . . . .	16.0
Conversion to acetaldehyde . . . . .	3.5
Hydrogenation to alcohol (including 20,000 cub. ft. electrolytic hydrogen) .. . . .	6.5
	<hr/>
	£26.0

or an approximate cost of 2s. per gallon of alcohol.<sup>19</sup>

The economically successful operation of this process rests, apparently, therefore, on the relative cost on the one hand of calcium carbide and on the other of grain or cellulose material suitable for conversion into alcohol by fermentation; and it seems likely that, other than in exceptional localities, the balance will remain in favour of fermentation processes, at all events in the immediate future.

*Isopropyl alcohol* has come into favour of late years as a substitute for ethyl alcohol in the production of perfumes; it can be made from acetone at a price which compares more or less favourably with that of ethyl alcohol. Acetone, produced either by fermentation from starch or chemically from acetic acid, is mixed with excess of hydrogen and passed over nickel, as in the preceding case, but at a temperature of 150°–180°. The process is conveniently carried out under pressure, when the rate of reaction and the ease of condensation of the isopropyl alcohol produced are both increased. By employing high pressures it should be readily possible to effect hydrogenation of acetone in the liquid condition at, say, 120°–140°, but so far as we are aware, isopropyl alcohol at present manufactured by this method is produced by catalysis in the vapour phase.

*n-Butyl alcohol*, which is now a very important solvent as well as forming several esters of importance as plasticisers and fixatives, is not only produced by fermentation (Section III, Chapter IV, p. 349) but also from acetaldehyde. The aldehyde is converted into aldol and thence into crotonaldehyde (Section IV,

Chapter I, p. 379), which yields *n*-butyl alcohol by hydrogenation. The hydrogenation of crotonaldehyde is frequently conducted in the vapour phase, a mixture of hydrogen and the aldehyde being passed over a nickel catalyst at about  $170^{\circ}$ – $220^{\circ}$ , usually at a pressure greater than atmospheric. Reduced nickel chromate<sup>20</sup> and copper silicate<sup>21</sup> have been mentioned as suitable forms of catalyst for the vapour process. As in the case of acetaldehyde, excess of hydrogen and the presence of a certain proportion of steam as an inert diluent might be expected to assist the process by retarding the formation of by-products.

## (ii) METALLIC OXIDES AS CATALYSTS

In the processes discussed above the catalytic agent was a metal prepared in suitable form. In a number of cases, however, oxides of the metals exert specific influence on the course of chemical change, and a few of these are used, although not so widely as metal catalysts, on a manufacturing scale.

Often the action of a metallic catalyst is connected to some extent, although not exclusively, with its capacity for adsorbing hydrogen, so that catalyses by metals can usually be placed in the categories of hydrogenation or dehydrogenation. The metallic oxides display little tendency to act simply as hydrogenating or dehydrogenating catalysts; they are more usually concerned either in the removal of the elements of water from organic compounds or in processes of more or less simple oxidation (as distinct from dehydrogenation)—processes, for example, such as the oxidation of hydrogen sulphide to sulphur or sulphur dioxide (*cf.* Chapter IX, p. 233) and of aromatic hydrocarbons to oxygenated derivatives.

The extent to which such processes are used at the present time varies very considerably. Some indication of the possibilities of this type of contact action will be

gathered from the typical cases which are discussed briefly in the present and preceding chapters.

It should be pointed out here that quite a number of processes in which metallic oxides are employed as catalysts of hydrogenation have already received notice in Chapters II, III and IV of this Section. The most important of these are : iron oxide-iron in the water-gas-steam reaction, zinc-chromium oxide in the synthesis of methanol, molybdenum oxide in the hydrogenation-cracking processes, and the mixed metal oxide-metal catalysts used in the Fischer-Tropsch conversion of water-gas into hydrocarbons.

#### Dehydration of Alcohols to Olefines or Ethers.

In the later stages of Sabatier's investigations on the catalysis of organic compounds at solid surfaces, attention was paid to the dehydrating and dehydrogenating activity of a large number of metallic oxides. This aspect of the subject was especially studied by Sabatier and Mailhe,<sup>22</sup> who found that, for example, ethyl alcohol was converted into ethylene and water or, alternatively, into hydrogen and acetaldehyde, by the oxides quoted in the following table. The third column

		Per cent. $C_2H_4$ .	c.c. per min.
Thoria . . . . .	$ThO_2$	100	31
Alumina . . . . .	$Al_2O_3$	98.5	21
Oxide of Tungsten (blue) . . . . .	$W_2O_5$	98.5	57
Chromium oxide . . . . .	$Cr_2O_3$	91	4.2
Silica . . . . .	$SiO_2$	84	0.9
Titania . . . . .	$TiO_2$	63	7
Zirconia . . . . .	$ZrO_2$	45	1
Uranium oxide . . . . .	$UO_2$	24	14
Ferric oxide (initial) . . . . .	$Fe_2O_3$	14	32
Vanadium oxide . . . . .	$V_2O_3$	9	14
Zinc oxide . . . . .	$ZnO$	5	6
Tin oxide (initial) . . . . .	$SrO$	0	45
Manganese oxide (initial) . . . . .	$Mn_2O_4$	0	12
Cadmium oxide (initial) . . . . .	$CdO$	0	11.2
Magnesium oxide . . . . .	$MgO$	0	Traces.



shows the percentage of ethylene in the mixture of gases produced when ethyl alcohol vapour was passed over the respective oxides at  $340^{\circ}$ – $350^{\circ}$ .

From this table it is clear that thoria, alumina, and the oxides of tungsten and chromium are pre-eminently dehydrating catalysts, whilst a large number of others promote both types of decomposition; finally a few oxides, notably those of zinc, tin, cadmium and manganese, are almost exclusively catalysts of dehydrogenation. From a technical standpoint it is necessary, of course, not only to consider the relative proportions of the two types of reaction, but also to bear in mind the intensity of the change set up by any given oxide. Again, those oxides which give rise to a mixed effect are obviously not likely to be suited to the production of a definite technical product, although it may be observed that so far as relative activity is concerned, some at any rate of this class are considerably more active than the hydrogenating oxides just mentioned. There remains the more or less exclusively dehydrating type of metallic oxide catalyst, and here certain of these (especially silica, alumina and thoria) are, when prepared with due regard to the condition of the exposed surface, of very high activity.

It should be made clear, however, that, so far as we are aware, none of these dehydrating oxides has been used hitherto in the manufacture of olefine hydrocarbons or ethers. When, for example, ethylene is required to be produced from alcohol in quantity, it is probably nearly always made by the catalytic action of sulphuric or phosphoric acids as described in Section IV, Chapter III, p. 418.\* The methods which are indicated below, therefore, are to be regarded rather as indications of procedure potentially available than of processes actually in being; consequently it

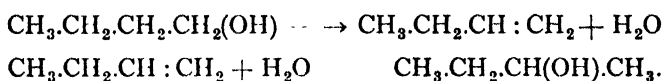
\* In practice it is rarely necessary to manufacture ethylene or other olefines from the alcohols. All the lower olefines are present in abundance in natural and cracked petroleum gases, and the present tendency is rather to convert these into alcohols and their derivatives (cf. Section IV, Chapter I, pp. 387–391).

is not necessary to discuss them at any length. The oxides employed by Sabatier and Mailhe were prepared as a rule by precipitation from the nitrate followed by washing and gentle heating, or, by gentle calcination of the nitrate of the metals. The work of Adkins<sup>23</sup> and his colleagues in America on the oxides of aluminium and titanium prepared by different methods, for example from inorganic salts, from the acetates or from ethylates (or other alkyl oxides) of these metallic oxides, showed that considerable differences, not only in the activity but also in the type of action induced, are to be observed according to the method of preparation of the oxide which has been followed. The exact implication of these variations is not fully understood, and reference may be made to the original communications of this author and to further discussion by H. S. Taylor<sup>24</sup> and others on the theoretical aspects of these observations.

Coming to practical details, it may be stated that at temperatures varying between  $330^{\circ}$  and  $450^{\circ}$ , ethyl alcohol is transformed more or less quantitatively into ethylene and water in presence of suitably prepared thoria, alumina or silica. Sabatier states that thoria is the most active oxide and also the most suitable under working conditions. Alumina comes next in the series; and it is probable that, if this process were required to be worked technically, economic considerations would decide the case in favour of the latter oxide. As in all similar cases, it would be necessary so to pre-heat the alcohol vapour that the temperature in the catalyst chamber itself would be maintained suitably constant and probably not below  $350^{\circ}$ . According to Sprent,<sup>25</sup> the net yield of ethylene from alcohol by the alumina process is greatest at  $360^{\circ}$ ; above this temperature the ethylene tends to be decomposed and also, the alumina catalyst slowly undergoes change of physical state, thus rendering the surface progressively less active.

It seems reasonable to suppose, in the case of ethylene,

that the heat consumption involved in this process must always be considerably greater than that in the alternative sulphuric or phosphoric acid process, which proceeds at about  $170^{\circ}$  or  $180^{\circ}$ , and for this reason one cannot foresee any extensive application of the metallic oxide process in this case. In special cases, however, the process might be technically feasible. Thus, in order to convert normal butyl alcohol into iso-butyl alcohol, it has been proposed<sup>26</sup> to pass the vapours of normal butyl alcohol over alumina at about  $400^{\circ}$ , when the hydrocarbon butylene is produced, and this by treatment with sulphuric acid and subsequent saponification furnishes the corresponding secondary or iso-butyl alcohol.



It is, of course, obvious that dehydration of alcohol can take place in two ways, giving either ethylene and water or ether and water. So far as the aliphatic alcohols are concerned, the production of ethers is decidedly the exception rather than the rule, although both Sabatier<sup>22</sup> and Ipatiev<sup>27</sup> state that in presence of alumina at low temperatures (*i.e.* below about  $250^{\circ}$ ) some ether is produced in addition to ethylene. The case is somewhat different, however, with aromatic alcohols and especially with phenols, and it was shown by Sabatier that passage of phenol vapour over thoria or alumina at  $400^{\circ}$ – $450^{\circ}$  resulted in the production of considerable amounts of diphenyl oxide (or diphenyl ether), a compound with a strong odour reminiscent of geranium leaves, and used to some extent as a synthetic perfume.

The Du Pont Corporation<sup>28</sup> has patented the catalytic production of aliphatic amines by passing the corresponding alcohol vapour with ammonia at  $250^{\circ}$ – $500^{\circ}$  over a porous rigid (silica) gel containing a dehydrating oxide such as alumina:

**Production of Ketones from Organic Acids.**

Metallic oxides have been used industrially from time to time in the catalytic manufacture of ketones from the simpler organic acids, especially of acetone from acetic acid. The general course of this change, which is a somewhat complicated case of dehydration, is summed up in the equation



This decomposition, of course, is familiar in the dry distillation of, for example, calcium acetate, when acetone, water and calcium carbonate are produced. As early as 1895, Squibb<sup>29</sup> suggested that this process could be made catalytic by passing a current of acetic acid vapour over barium carbonate at a temperature of about 500°. It was found that at least 90 per cent. of the theoretical yield of acetone could be obtained in this way, and the method found some technical application in the United States. Later, Ipatiev,<sup>30</sup> Sabatier, Mailhe and Senderens<sup>31</sup> showed that metallic oxides such as those of aluminium, thorium, chromium or zinc were equally effective at lower temperatures (400° or below). The French scientists also found that passage of a mixture of the vapours of formic and a higher aliphatic acid over alumina led to the production of the corresponding aldehyde; for example, a mixture of formic and acetic acids yielded a certain amount of acetaldehyde, an action which is again analogous to the preparation of acetaldehyde by distillation of a mixture of calcium formate and acetate.

The function of metallic oxide or carbonate catalysts in this action is thus strictly parallel with the corresponding decomposition of calcium salts of the same acids, and it may be taken for granted that transitory formation of the salt concerned takes place at the catalyst surface or, at least, that selective adsorption (in the chemical sense) of the aliphatic acids takes place at the metallic oxide surface.

*Technical Production of Acetone over Metallic Oxide Catalysts.*—As already stated, Squibb's process has been used on a technical scale, employing barium carbonate at  $500^{\circ}$ . The plant used in one form of this process consisted of a rotary kiln 2 ft. in diameter and 12 ft. in length, containing a layer of precipitated barium carbonate and maintained at  $450^{\circ}$ – $500^{\circ}$ ; this plant was capable of converting 1,700 lb. of glacial acetic acid into acetone in 126 hours with a yield of about 90 per cent. In a later form of catalytic process, the catalyst consisted of alumina precipitated or impregnated on a porous granular support, and somewhat similar results to the Squibb process were obtained at about  $480^{\circ}$ – $500^{\circ}$ ; a plant of this type, producing two to three tons of acetone per day, was operated for a time during the war of 1914–1918.

The Canadian Electrochemical Products Company at Shawinigan has used a somewhat similar process (referred to again in Section IV., Chapter I, p. 387) with synthetic acetic acid produced from acetylene; the vapour of the acid was led over a catalyst, which consisted of calcium hydroxide with a small quantity of magnesium hydroxide coated on rough cast-iron balls and contained in steel tubes 13 ft. long and 1 ft. in diameter. By careful control of the temperature, both in pre-heating the acetic acid vapour and in the catalyst chamber itself, it was found possible to obtain 95 per cent. conversion to acetone at  $483^{\circ}$ .

It is doubtful whether much, if any, acetone is made by these processes at the present time, but this is due solely to the circumstances that acetone is available from the fermentation of carbohydrates by means of specific bacteria (*cf.* Section III, p. 349), and is also produced directly from alcohol (or acetylene) and steam in one operation by passage over special mixed catalysts (p. 260). The fermentation process produces for every part of acetone two parts of *n*-butyl alcohol, a material, which is at present in very considerable demand, so that here acetone may be looked upon as a

by-product resulting from the manufacture of butyl alcohol. The direct catalytic process from alcohol (or acetylene) and steam gives acetone in a yield which compares economically with the overall-yield when it is made catalytically from either source by the three-stage process (through acetaldehyde and acetic acid).

The investigations of Sabatier and Ipatiev show that other higher ketones may be produced in the same way, but there is little or no technical demand for most of these. It may, however, be mentioned that, as Easterfield and Taylor have shown,<sup>32</sup> the higher fatty acids (for example, palmitic or stearic acid) can be converted in high yield into the corresponding ketones by agitating them in the liquid state at about 300° with siliceous materials, alumina or, preferably, ferrous oxide, whilst Grün<sup>33</sup> states that the action proceeds readily enough in presence simply of massive iron. The ketones thus produced are solids of fairly high melting-point (*e.g.*, from 60°–85°), and may well find application as waxes for various purposes, for which their texture, relative high melting-point, and completely neutral nature would seem to render them suitable; catalytic reduction of the liquid ketones converts them into the corresponding secondary alcohols, which are also wax-like bodies.

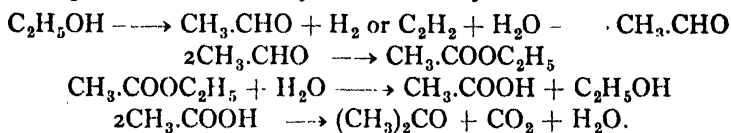
Sabatier and his co-workers, again, indicate that aromatic acids can be converted in the vapour phase to the corresponding ketones, but the action apparently proceeds with considerably less ease in the case of these compounds.

#### Direct Catalytic Production of Acetone from Alcohol or Acetylene and Steam.

It has been found that the sequence of actions alcohol (or acetylene) → acetaldehyde → acetic acid → acetone can be achieved in one process providing that a suitable mixed catalyst is employed. During the past decade this single-stage process has been brought to a high state of efficiency and has now practically

superseded the technical catalytic conversion of acetic acid into acetone. Various mixed catalysts have been proposed for the single-stage process, and that most often used in practice is probably a mixture of reduced iron oxide or metallic iron to which has been added a small proportion of a mild alkali—potassium carbonate or calcium oxide.

The action comprises the following consecutive transformations of alcohol (or acetylene), all of which take place concurrently in the catalyst chamber :—



Kagan, Sobolev and Lubarski<sup>34</sup> have recently established that ethyl acetate is produced immediately when acetaldehyde is passed over various mixed catalysts at 300°–350°, and that, while anhydrous ethyl acetate is decomposed at 400° by a zinc-chromium oxide catalyst into acetone, ethyl alcohol, ethylene and carbon dioxide, hydrolysis of the ester is involved when steam is also present. The whole process (from alcohol) may be summed up by the approximate equation :—



The yield of acetone obtained in the technical process usually amounts to at least 80 per cent. of that shown in the equation. When, as in England, alcohol is used as raw material, the gaseous products of the reaction consist of a mixture of 80 per cent. hydrogen and 20 per cent. carbon dioxide; after removal of the latter, the hydrogen is suitable as regards purity for use in catalytic hydrogenation. Thus, if alcohol is being converted in the same factory into acetone by the above process, and into acetaldehyde by combined dehydrogenation and oxidation (p. 247), the hydrogen produced during either or both of these processes is at hand for subsequent hydrogenation of crotonaldehyde (from acetaldehyde) to *n*-butyl alcohol.

The mixture of alcohol vapour or acetylene with about 4-5 volumes of steam is preheated (using heat-interchange) to about  $400^{\circ}$  and passed through tubes packed with the pelleted or metallic catalyst at about  $450^{\circ}$ ; the emerging gases, after giving up most of their heat in the interchangers, are passed to condensers and then through water-scrubbers, the acetone being rectified by distillation and the permanent gases collected for further purification of the hydrogen. As already mentioned, the most usual catalyst is probably rusted iron scrap, or reduced iron oxide, which has been mixed with a solution of potassium carbonate or calcium acetate. The earliest patents<sup>35</sup> of the Holzverkohlungs-Ind. A.-G. dealing with this process suggest passage of acetylene and steam at  $470^{\circ}$ - $500^{\circ}$  over iron oxide (in the form of superficially rusted iron shavings, or iron shavings coated with iron oxide and manganese oxide or with iron oxide and barium carbonate), and of alcohol, acetaldehyde or ethyl acetate mixed with steam at about  $500^{\circ}$  over a catalyst made by evaporating a stirred mixture of calcium acetate solution and rusty iron shavings. A later patent<sup>36</sup> proposes the combination of the exothermic conversion of acetylene into acetone with the non-exothermic conversion of alcohol into acetone, and states that the latter is produced in 89 per cent. yield when a mixture of alcohol vapour, acetylene and steam is led over rusty iron sponge containing 3 per cent. of manganese oxide at  $470^{\circ}$ ; mixed catalysts comprising oxides or carbonates of nickel or cobalt, preferably with iron oxide, together with oxides of alkaline earth or other light metals, have also been suggested.<sup>37</sup> British Celanese Ltd. *et al.*<sup>38</sup> propose to prepare a mixed catalyst by heating, for example, an alkaline earth oxide with a feebly acidic oxide ( $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$  or  $\text{ZnO}$ ) at  $1,400^{\circ}$ - $1,600^{\circ}$  to give a product which, after powdering, sets by addition of water; a lime-zinc oxide "cement" catalyst of this type gives a yield of 60-70 per cent. of acetone from alcohol and steam at  $465^{\circ}$ - $480^{\circ}$ .



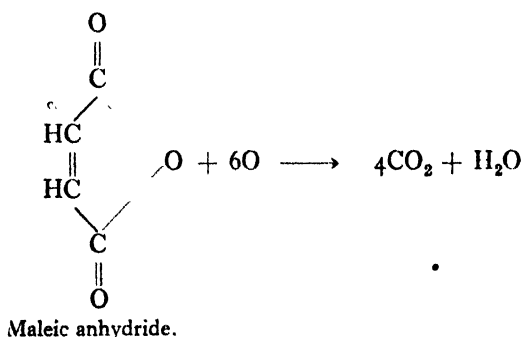
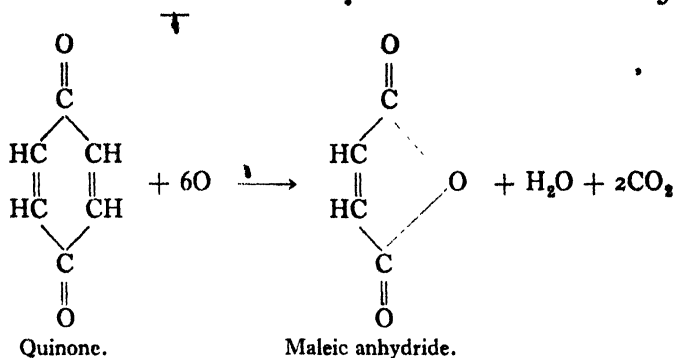
### Oxidation Processes—Oxidation of Hydrocarbons in Presence of Metallic Oxides.

The group of processes about to be described has only been investigated systematically since about 1916, but it would appear that many important reactions may well be developed in the future on the basis of the work which has been carried out during that period, notably by the Barrett Co. of New York, Weiss and Downs, the British Government Department of Scientific and Industrial Research, and other groups of workers.

The work of the D.S.I.R. has dealt largely with the possibilities of oxidising simple aliphatic hydrocarbons, such as those present in fuel gases, in order, for example, to produce formaldehyde. A report on the general results obtained has been published by Ledbury and Blair,<sup>39</sup> who show that, so far as this particular proposition is concerned, it does not appear that there is any immediate likelihood of the formaldehyde produced in this way competing with that produced from coal through the intermediate agency of water-gas and methyl alcohol.

The phase of these processes which is at present most interesting is that of the controlled oxidation of aromatic hydrocarbons into products of technical value, by passage of a mixture of the hydrocarbon vapour with air over certain metallic oxides, especially those of vanadium and molybdenum. It has been known for many years that vanadium oxide has the property of effecting oxidations of this character. In 1892, Walter<sup>40</sup> stated that in presence of air and vanadium oxide toluene could be converted into benzaldehyde or benzoic acid and anthracene into anthraquinone, and at a considerably later date (1904) he patented a number of catalysts suitable for this reaction. He also stated that, in addition to the above reactions, alcohol could be oxidised to aldehyde and acetic acid, benzene to diphenyl, naphthalene to  $\beta$ -naphthol, diphenylamine to carbazole, etc. Somewhat later, Woog<sup>41</sup> observed





In the ordinary combustion of benzene it is probable, in fact almost certain, that these intermediate products are formed, but at the temperature of active combustion the speed of the final reaction is as great or greater than that of the intermediate phases. If, however, the amount of oxygen present with the benzene is suitably adjusted and reaction is made to take place at a relatively low temperature, for example, at  $350^{\circ}$ – $450^{\circ}$  at the surface of an appropriate material, the products depend largely on the nature of the latter substance. Weiss and Downs classify catalysts as "productive catalysts" and "active catalysts"; the latter term refers to substances which substantially yield only completely oxidised products (they mention, for example, that whilst platinum is very highly active, it tends to produce the completely oxidised materials, *i.e.*, carbon dioxide and water). The "productive catalysts," on the other hand, are those which under suitable conditions lead

mainly to an intermediate stage, so that a relatively high yield of a desired intermediate oxidation product can be successfully isolated. The first step in the systematic investigation, therefore, was to select suitable "productive catalysts." Vanadium oxide appears at present to be the preferred material, with molybdenum oxide a good second. Subsequent stages in the working out of the process consisted in the elaboration of a laboratory apparatus, and finally a technical plant, in which the temperature conditions and the proportion of air to hydrocarbon vapour could be maintained so as to give maximum efficiency in the process.

The large-scale unit described by Weiss and Downs<sup>45</sup> consists of a multiple form of their individual laboratory type of catalyst tube. The latter is a square  $\frac{3}{8}$ -inch steel tube sufficiently long to contain a layer of the catalyst, and also to allow for pre-heating of the entering gases. Thus the tube may be 10 in.-1 ft. in length, and contain a layer of 4-5 in. of catalyst supported towards its lower end. Great stress is laid upon the necessity for avoiding any development of local high temperatures in the catalyst mass. The whole aim of the design of this apparatus is to secure rapid removal of heat as fast as it is developed by the oxidation process. To this end, the catalyst itself consists of granules of aluminium which are coated with vanadium oxide, whilst the space above the catalyst may also, if desired, be filled with untreated aluminium pellets in order to assist in the conduction of heat. Further, the temperature is regulated very skilfully by enclosing the catalyst tube in an ordinary cylindrical tube provided with a header pipe. This tube is filled with mercury to a level a little higher than that of the catalyst in the inner tube. To start the reaction, the mercury is boiled and a mixture of, say, benzene and air in the correct proportions is passed downwards through the catalyst tube. As soon as oxidation sets in, the heat developed exothermally is

in excess of that required to maintain the desired temperature at, say,  $400^{\circ}$ , but is rapidly conducted to the mercury and dissipated in boiling the latter, the vaporised mercury being again condensed in the upper part of the apparatus as it pre-heats the interacting benzene-air mixture. Removal of the heat of reaction in this way (as latent heat of evaporation of a liquid boiling at or near the desired temperature) guarantees that the catalyst tube will be surrounded by a heat-removing bath, the temperature of which is the same at all points. Hence each tube operates exactly like its companions, and the results in a single laboratory tube can be duplicated in a plant converter where there are, say, a thousand tubes. This method is therefore superior, in the case of an exothermal action, to supplying heat by means of a bath of lead or other high-boiling liquid.

To avoid the high cost of pure mercury in the heating system, an amalgam with a cheaper metal may be utilised, providing that it is liquid below the temperature at which the catalyst must be maintained, and that only the mercury is vaporised. The following amalgams have been suggested: mercury-lead,<sup>46</sup> 75 per cent. mercury-25 per cent. cadmium,<sup>47</sup> 40 per cent. mercury-30 per cent. tin-30 per cent. lead.<sup>48</sup> Various devices for promoting circulation of the liquid metal in the heating tubes and for improving the heat transfer between the catalyst and the mercury vapour and bath have also been put forward.<sup>49</sup>

The most recent form of plant converter for this oxidation process is described as consisting of a nest of many catalyst tubes of the above type, set into perforated plates and surrounded by the cylindrical jacket of the converter, the interstices between the tubes and the jacket being employed as the vapour bath consisting of mercury or, according to a later suggestion, of melted sulphur. In order to obtain the minimum volume of mercury or sulphur and also to obtain the maximum volume of catalyst, square tubes are employed to hold the catalyst; this has the further advantage

that heat can be removed more efficiently since the ratio of tube surface to catalyst volume is much greater in a square tube than in a round tube. The cylindrical jacket enclosing the nest of tubes is connected to two or more pipes at its upper end, which act as reflux condensers for the mercury or sulphur vapour, and by means of which, if necessary, nitrogen can be admitted under pressure, so that, within limits, the boiling point of the bath can be raised to any desired temperature above the normal boiling point of the liquid at atmospheric pressure. The hydrocarbon-air mixture enters at the top of the catalyst tubes, is pre-heated in the upper part of the latter, and passes over the catalyst in the lower part, the gaseous products of the reaction passing from the base of the vessel to fractional condensers, water scrubbers, etc., in which the products and unchanged raw material are separated and recovered. The losses of mercury or sulphur by vaporisation are exceedingly small, and hardly contribute anything appreciable to the running costs.

A converter of this type with outside dimensions 3 ft. in diameter by 4 ft. high, and containing a nest of  $\frac{5}{8}$ -in. square tubes spaced  $\frac{3}{16}$  in. apart, will produce a ton of phthalic anhydride from naphthalene in twenty-four hours.

The Selden Co. and A. O. Jaeger<sup>50</sup> have patented the use of vanadium pentoxide-zeolite catalysts in the oxidation of organic compounds with air. Such catalysts may contain the vanadium oxide in chemical combination with the zeolite (by base exchange replacement of an alkali in the original zeolite) or the vanadium oxide may be deposited on the zeolite, the latter acting simply as a catalyst support. The latter form of catalyst is preferred for the oxidation of organic compounds. The same patentees<sup>51</sup> have also claimed that the addition of certain "stabilisers" to the catalyst leads to better control of the reaction. Many salts of oxides not reducible by hydrogen seem to fulfil the function of stabiliser, and the addition of

sulphates, or the heating of vanadium oxide, mounted on kieselguhr or zeolite, at  $400^{\circ}$ – $500^{\circ}$  in burner gases to convert free alkali into sulphate, is specifically mentioned.

Maxted<sup>52</sup> found that tin vanadate is more suitable than vanadium oxide alone in the oxidation of organic compounds, since it is effective at  $250^{\circ}$ – $300^{\circ}$ , *i.e.*, at least  $100^{\circ}$  lower than vanadium oxide itself. He obtained, for example, 84.3 per cent. yield of phthalic anhydride from naphthalene at  $280^{\circ}$ , 59 per cent. yield of phthalic anhydride from *o*-xylene at  $290^{\circ}$ , and 57 per cent. yield of benzoic acid from toluene at  $290^{\circ}$ . *p*-Nitro-, *o*-bromo- and *o*-chloro-toluenes gave smaller yields (14–24 per cent.) of the correspondingly substituted benzoic acids. Bismuth vanadate is almost equally effective in some cases. So far as we are aware, however, the use of metallic vanadates in place of vanadium oxide has not yet been adopted in large-scale practice.

As in all other cases of industrial catalysis, the efficiency of the process depends entirely on the construction of large-scale converters, the design of which takes into account all the specific chemical factors of the particular operation. Thus, for example, Weiss and Downs find that in large-scale practice, correctly prepared forms of vanadium oxide possess a long life, acting satisfactorily for at least six months of continuous operation, during which time the amount of phthalic anhydride, for instance, produced is at least 20,000 times the weight of vanadium oxide present. The question of catalyst replenishment accordingly becomes of little practical importance; when at length it is desirable to replace a partially de-activated catalyst with a fresh charge, the vanadium oxide in the spent material is, of course, recovered by chemical means and the recovered vanadium solution employed in the production of new catalytic material.

It will be seen that processes of controlled oxidation

in the vapour phase at the surface of suitable catalysts have become of great importance in the manufacture of several industrial organic chemicals, and may be expected to find increasing application in the future. Undoubtedly the most important instance is the production of phthalic anhydride from naphthalene. This is now conducted almost universally in vanadium oxide catalytic plants, which have been erected extensively in Germany and in this country, as well as in the United States. The process is also being used increasingly in Europe in the manufacture of anthraquinone from anthracene and of benzaldehyde and benzoic acid from toluene.

The extent to which these processes had already developed in the United States by 1926 will be gathered from the following extract from the paper by Downs in that year :—

“ Since the discovery by H. D. Gibbs of the vapour-phase catalytic production of phthalic anhydride from naphthalene in 1916, its production has expanded rapidly, until to-day it is being made in the United States at the rate of more than four million pounds per year. Most of this production is being consumed in the preparation of anthraquinone by condensing it with benzene in the presence of aluminium chloride and later treating the benzoylbenzoic acid thus formed with concentrated sulphuric acid. Anthraquinone made in this way is of a very high degree of purity. Methyl-anthraquinone and chloro-anthraquinone are similarly made. A yield of more than 80 lb. of phthalic anhydride per 100 lb. of naphthalene fed to the converter is obtained. By catalytic oxidation of toluene, benzaldehyde and benzoic acid free from chlorine can be made in a high state of purity.

“ Anthraquinone can be made from crude anthracene. During its synthesis, the impurities such as phenanthrene and carbazole are burned up. The production of anthraquinone by this process depends upon the economics of the process compared with its synthesis from phthalic anhydride. The cost of anthracene with no credit for the carbazole produced as a by-product is excessive in the United States, but the opportunities for the success of the process abroad are good.

“ Maleic acid can be produced at a yield greater than 60 lb. per 100 lb. of benzene fed to the converter. The acid itself is not ordinarily recovered and sold as such, but is converted with theoretical yields into malic acid, by autoclaving in aqueous solution. Malic



acid is a perfect substitute for citric acid, and in many respects is superior to tartaric acid as an organic acidulant. Other derivatives such as esters and condensation products heretofore unavailable can be made from maleic acid."

It is likely that, if maleic anhydride can be produced sufficiently cheaply from benzene by catalytic oxidation, a considerable use could be found for it in refining crude benzols from cracked spirit, the di- or poly-ene impurities therein (which give trouble owing to gum-formation) being removable by Diels-Alder condensation with maleic anhydride.<sup>53</sup>

Another use suggested<sup>54</sup> for this process is in the conversion of tar oils into benzene and its homologues for use in motor fuels. The tar oil fraction boiling between  $200^{\circ}$  and  $260^{\circ}$ , when vaporised with air over vanadium pentoxide at  $440^{\circ}$ , is converted into naphthalenes and alkylnaphthalenes and thence into a mixture of phthalic and methylphthalic acids; the latter are decarboxylated by autoclaving at  $420^{\circ}$  with traces of caustic soda. In this way the tar oil fraction mentioned can be converted into about 24 per cent. of its weight of benzene and homologues.



## CHAPTER XI

### HYDROGENATION OF LIQUID ORGANIC COMPOUNDS IN PRESENCE OF REDUCED METALS

NEARLY all organic compounds which contain ethylenic or acetylenic linkages, the benzenoid ring-system of many aromatic compounds, and many aldehydes or ketones undergo addition of hydrogen when treated in the liquid condition with gaseous hydrogen in presence of certain finely divided reduced metals under appropriate conditions of temperature and pressure.

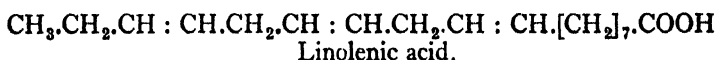
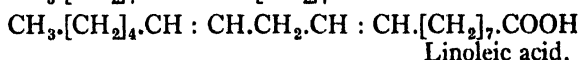
The metals in question include palladium, platinum, nickel, cobalt and copper, but so far as industrial work is concerned, nickel is by far the most commonly employed, the noble metals being perhaps employed to a minor extent in the production of a few drugs and fine chemicals by hydrogenation.

The many potential applications of this method to industrial uses have, so far, been limited in practice by economic considerations to a very few instances: the hydrogenation or hardening of liquid fatty oils, the production of hydroaromatic derivatives from phenol, the cresols, and naphthalene, and the manufacture of a few isolated chemicals useful in pharmacy, perfumery, etc., of which the production of menthol from thymol or from piperitone may be given as an instance. Of these applications, the output of hydrogenated fats greatly exceeds the rest, in consequence of the wide scope for hardened fats in soaps, candles and also in edible products, and of the relatively low hydrogen consumption, much less hydrogen being required to produce an equal weight of finished product from fats than from phenol, naphthalene, or other organic compound of comparatively small molecular size.

**The Hydrogenation of Fats.<sup>1</sup>**

Solid fats are of economic value as edible products, soaps, or candles, and the quantities required for these purposes are in the aggregate far greater than those of the liquid fats, or fatty oils, whose main outlets (in addition to soap) are for paints, lubricants, burning oils, leather-dressing, etc. Contrariwise, liquid fats preponderate in nature over those which are solid at ordinary temperatures, and the latter accordingly tend normally to be more valuable and possess a higher market value. Consequently it was attempted for many years to evolve a technical process for converting liquid into solid fats, or, as it was more usually termed, to transform oleic into stearic acid.

Broadly speaking, the main difference between solid and liquid natural fats or glycerides is the relative abundance in the latter of glycerol esters of the unsaturated oleic acid, or its still more unsaturated analogues, linoleic and linolenic acids :—



The natural fats of higher melting-point contain relatively more of the higher saturated acids (in combination with glycerol), for example :—



Obviously reduction of (*i.e.*, addition of hydrogen to) glycerides of the former acids would furnish the corresponding derivatives of the solid stearic acid (m.p.  $71^\circ$ ), and so numerous attempts, none of which led to technical success, were made in the past fifty or eighty years to carry out the transformation of unsaturated into saturated acids. Thus it was proposed to heat oleic acid with phosphorus and iodine ; or to

fuse it with caustic potash, when palmitic acid is formed (this was actually put into practice by Radisson at Marseilles for some years);\* or to convert it into solid hydroxystearic acid and stearylactone by heating with zinc chloride (Benedikt) or with sulphuric acid (Geitel).

Sabatier,<sup>2</sup> however, in the course of his classical work on the catalytic hydrogenation of the vapours of organic compounds in presence of nickel, observed that oleic acid vapour was thus transformed into stearic acid; but he believed that hydrogenation only occurred in the state of vapour. Fokin also showed that oleic acid vapours were converted by hydrogen in presence of platinum into stearic acid.

The successful technical operation of a vapour hydrogenation process for oleic acid (b.p.  $290^{\circ}/100$  mm.) would be exceedingly difficult, whilst that of the non-volatile glycerides is of course out of the question; but, shortly after Sabatier's discovery, Normann<sup>3</sup> took out a patent in Germany in 1902 for the hydrogenation of unsaturated fats in the liquid state, and this process was the foundation of technical fat-hydrogenation. In the course of the next decade the observation of Normann was developed in several quarters into a process suitable for large-scale working, and by about 1910 the output of hydrogenated fats—chiefly hardened whale oil—probably amounted to several hundred tons per week. Since, at that period, the difference between the market prices of tallow and of whale and a few other liquid oils was about £15–£25 per ton, the process offered considerable attractions, and capacity was rapidly extended until, by the end of the war period of 1914–1918, the world's potential output of hardened fats had reached many thousands of tons per week. Several of the existing hydrogenation plants in this country, on the Continent, and in America are each able to deal with as much as 1,000 tons of fat per week.

Consideration of the theoretical side of industrial

catalysis, which was dealt with in Section I, will cause the reader to appreciate that the work involved in developing fat-hydrogenation has contributed useful data in connection with the mechanism of heterogeneous catalytic actions ; it should also indicate the complexity of the practical issues which were faced by the pioneers of fat-hydrogenation at a time when theoretical knowledge of contact action was by no means so far advanced as at the present day. The practice of fat hardening is complicated further by the fact that, in addition to the actual hydrogenation process, the production of hydrogen of a definite standard of purity, the production of active catalyst and its recovery after use, and the removal of impurities from the oils treated have all to be carefully considered. A fat-hydrogenation plant is thus somewhat costly from the point of view of initial capital expenditure, and the process tends to be concentrated in units of fairly large size, and, as a general rule, is conducted only by concerns of some magnitude.

In the actual hydrogenation, several types of apparatus are in general use, and these may be classified broadly as follows :—

(i.) The *agitation system*, in which mechanical agitation is used to produce an intimate mixing of nickel, fatty acid and hydrogen ;

(ii.) The *circulation process*, in which a mixture of oil and catalyst is withdrawn from the lower part of the reaction vessel and injected as a fine spray into the gas-space at the top of the vessel by means of a pump ;

(iii.) The *continuous process*, in which oil passes downwards over a special type of stationary or massive catalyst and meets an upward current of hydrogen.

The details of the catalyst production and other features vary somewhat in these different systems, but in all cases the ancillary operations mentioned above have to be considered, and may be dealt with conveniently at this point before describing the actual hydrogenation process.

**Hydrogen Production and Purification.**

The amount of hydrogen fixed by different fats is, of course, dependent on their original state of unsaturation, and on whether they are to be converted into hard tallow-like fat, soft fat, or semi-liquid fatty oils. An average figure for hydrogen consumption over the usual range of oils dealt with in a fat-hardening installation is about 1 per cent. by weight of the fatty oil treated, or about 4,000 cub. ft. of hydrogen per ton of oil. It is not usually economical to conduct a hydrogenation plant on the agitation or circulation systems on an output of less than 200 tons per week, so that the minimum consumption of hydrogen is in the region of 800,000 cub. ft., and may be four or five times as much as this in a large plant.

Electrolytic hydrogen is best suited for fat-hydrogenation owing, of course, to its freedom from sulphur compounds and carbon monoxide. It is used to a considerable extent, even in this country, especially in locations where the oxygen simultaneously liberated finds an economical use. Since compression of the gas to high pressures is not required in fat-hardening installations, hydrogen is produced from water-gas by the intermittent processes described in Section II, Chapter II (pp. 88-89) rather than by the catalytic process. The hydrogen so produced is freed from sulphur compounds and contains only about 0.2 per cent. of carbon monoxide, a proportion which can be tolerated in the ordinary methods of catalytic fat-hydrogenation. A recent report<sup>4</sup> states that, in the United States, most of the hydrogen used for hardening fats is also made by the steam-iron process; electrolytic processes are, however, steadily advancing.

The following notes may be added here on the subject of purification of hydrogen for use in fat-hydrogenation:—

(a) *Sulphur Compounds.*—These include hydrogen sulphide and volatile compounds containing sulphur

and carbon, such as carbon disulphide and carbon oxysulphide, COS ; complete elimination of the latter substance offers considerable difficulty.

The crude hydrogen is usually first passed through a series of scrubbing boxes containing wet hydrated iron oxide, as in the case of water-gas or coal-gas, and this procedure effects fairly complete removal of free hydrogen sulphide, whilst some of the organic sulphur compounds are also trapped. To reduce the sulphur content of the gas to a minimum, however, it is necessary to submit the partially-cleansed hydrogen to further scrubbing, either by passage through slaked lime, or through a solution of caustic soda. The hydrogen should then be sufficiently free from sulphur compounds to be suitable for use.

(b) *Carbon Monoxide*.—This is still more difficult to eliminate completely, and it may be pointed out here that it is quite possible, and is indeed a frequent practice, to operate with hydrogen containing small proportions of this gas (*e.g.*, below 1 per cent.). The action of carbon monoxide as a catalyst "poison" is somewhat different from that of sulphur compounds. Hydrogen sulphide, for example, is exceedingly strongly adsorbed by nickel, and also tends to pass beyond the adsorption stage to direct chemical combination and production of nickel sulphide ; the adsorption by nickel of carbon monoxide, although very marked, is more comparable with that of the unsaturated organic compounds to be hydrogenated, and the main result of the presence of a reasonably small concentration of carbon monoxide is to slow down, rather than to suppress, hydrogenation of the fats. Moreover, the toxic effect of carbon monoxide declines considerably with increase of temperature, and the use of hydrogen containing this impurity can be compensated for to some extent by employing a higher working temperature.

When necessary, carbon monoxide may be eliminated, or reduced in quantity, in technical practice by



one of the three methods described in Chapter III of this Section (p. 102).

**Purification of Fats prior to Hydrogenation.**

It is also necessary that fats which are to undergo hydrogenation should be reasonably free from impurities prejudicial to the catalyst. In decreasing order of toxicity to catalytic nickel, the impurities likely to be present are organic sulphur compounds, oxidised unsaturated fatty compounds, whether degradation products (fatty acids of low molecular weight) or complex oxygen addition-products of a peroxidic or "linoxyn" type, colloidal suspensions of mucilage, protein, etc., moisture, and free higher fatty acids.

Free fatty acidity (up to about 3 per cent., and if the acids are those originally present as glyceride in the natural fat) does not hinder the course of hydrogenation to an uneconomic extent, and oils of this degree of acidity may be treated without preliminary neutralisation of the free acids.

Moisture is avoided as far as ordinary precautions may be taken, although it is unnecessary to attempt to maintain a rigidly anhydrous condition. The nickel, especially if supported on materials which are good adsorbents for water, tends to adsorb moisture preferentially to fat and, even at the temperature of reaction, may retain an adsorbed film of water which hinders contact between liquid fat and the catalytic metal.

The other impurities mentioned are toxic even in small concentration, owing to their adsorption by the nickel in preference to that of the unsaturated fatty compounds.

Organic sulphur compounds are found but rarely in neutral fats, although sulphur may be present owing to the oils having been extracted by carbon disulphide; it is not usually necessary, however, to employ oils extracted by this solvent for hydrogenation. Organic sulphur compounds are somewhat difficult to remove adequately in technical practice.

Oxidised glycerides and colloidal or other mucilage are generally removable by refining the fat either with aqueous caustic alkali or by agitation with a mineral earth or decolorising charcoal.

#### Catalyst Production.

For the purpose of general description it is sufficient to indicate the different forms of nickel which have been proposed for use in fat-hydrogenation—or rather, to make a judicious selection from the enormous variety of proposals existent in the patent literature of the subject.

The technical use of metals other than nickel in fat-hardening is confined practically to that of the rare metals palladium and platinum, which were formerly recommended on the score of relative activity and also because it was held that they could be employed at a substantially lower temperature than nickel. For technical purposes it is not practicable to use the delicate but unstable metal sols, which are effective at little above room-temperature, and so the palladium or platinum is supported on an inert material such as light magnesia.<sup>5</sup> In this condition the necessary temperature is appreciably higher than in the sol form, and the working temperature of nickel catalysts can, if necessary, be reduced to much the same degree as that of the noble metals, of course with proportionate diminution in the rate of hydrogenation. This consideration, together with the fact that any greater activity possessed by palladium or platinum as compared with nickel is more than offset by the difference in cost of the metals, has led to the use of the rare metal hydrogenating catalysts being restricted to a few special cases, relatively insignificant in total output.

The form of nickel catalyst employed depends to a large extent on the actual procedure followed in hardening the fat—in the continuous method it is necessary to have a massive or granular form of catalyst, but in

the other methods a more or less finely-divided substance is desirable. In either case it is of course essential to secure that a reasonable degree of activity is possessed by the catalyst and that the activity should not decline with undue rapidity, whilst in the case of powdered catalysts it is necessary to have these in a form which permits of complete and easy separation from the hardened fat by means of filtration.

From the theoretical principles mentioned in Section I (pp. 22, 39), it will be obvious that a smooth surface of metallic nickel, such as that of an electrolytically deposited film or smooth metal turnings, will possess quite negligible catalytic properties. On the other hand, Richardson <sup>6</sup> has shown that by sufficiently intense mechanical abrasion, nickel turnings can be made to acquire catalytic activity, the surface of the disintegrated metal becoming sufficiently "roughened" to produce the irregular or exposed conformation of nickel atoms which apparently conditions catalytic power. In 1925, Raney <sup>7</sup> showed that, when nickel-silicon or nickel-aluminium alloys were treated with caustic soda solution until all or most of the alloyed element was dissolved away, the residual nickel was in a very finely divided condition and possessed high catalytic activity, even at the ordinary temperature.

Bolton and Lush, <sup>8</sup> in their continuous hydrogenation process, use a catalyst in compact form which consists primarily of a mass of fine nickel turnings or nickel wool held in an openwork nickel frame. The surface of the nickel is rendered catalytic, either by immersing it as the anode in a dilute solution of sodium carbonate which is electrolysed at a suitable current density, or by steeping it in a bath of dilute sodium hypochlorite of definite concentration. The metal thus receives, by either process, a superficial coating of an adherent film of oxide which yields an active catalyst when, after washing and drying, it is replaced in the hydrogenation vessel and exposed to the action of hydrogen at about 250°.

In the discontinuous processes of fat hydrogenation the catalyst employed is frequently finely-divided nickel prepared by controlled reduction of the precipitated hydroxide or carbonate. As pointed out by Sabatier, Kelber <sup>9</sup> and others, completely reduced nickel powder itself cannot be exposed to a temperature much above 300° without loss of activity, whereas certain supported nickel catalysts will withstand a temperature of 500°. This is what is to be expected, since the irregular or exposed particles of nickel atoms at the surface are known to collapse or contract together at temperatures far below the ordinary "sintering" temperature of the metal; the interposition of irreducible atoms or molecules amongst the atoms of nickel may be supposed to restrain the cohesive forces which are mutually exerted by adjacent atoms of the metal itself.

Hence it is usual to mount the nickel on a support such as kieselguhr or charcoal, powdered pumice, powdered asbestos, powdered porous firebrick, silica gels, or the like; this practice not only increases the power of resistance to high temperatures, but also yields materials which are much more readily filtered and which can be washed with much greater ease prior to reduction.

Such catalysts, are prepared by precipitating a boiling solution of, for example, nickel sulphate, in which the support is suspended, with a slight excess of sodium carbonate, and thoroughly washing the precipitated carbonate on the support or carrier in order to remove all soluble salts. When washing is complete, the material is dried until friable and then reduced in a current of hydrogen at a suitable temperature, which may be from 300°–500° according to the support used. Obviously the reduced catalyst must not be exposed to atmospheric oxygen sufficiently to involve loss of catalytic activity by surface oxidation.

\* If a granular support such as pumice or fireclay is

employed, the resulting catalyst is suitable for continuous process work, but in practice the oxidised metal turnings referred to on p. 283 are more convenient.

In order to overcome the difficulty of handling reduced nickel catalyst in bulk, the reduction of suitable nickel compounds *in situ* beneath the oil which is to be hydrogenated, at about  $250^{\circ}$ , has been adopted in some factories. Bedford and Williams<sup>10</sup> recommended the reduction of nickel oxides, and Wimmer and Higgins<sup>11</sup> that of nickel formate in this manner, no support being necessarily employed. In recent years, both in Germany and in this country, the use of nickel formate as the source of catalyst has come into greater prominence. The simplicity of the reduction process counterbalances, to some extent, the greater cost of the formate, a quantity of which is suspended in some of the oil which is to be hardened and reduced therein by passage of a current of hydrogen through the stirred oil at  $240^{\circ}$ . When reduction is complete the oil with its charge of reduced nickel is cooled and mixed off with more of the oil to be hardened, the latter process being carried out at or below  $180^{\circ}$ . The concentration of nickel in the oil during the actual hardening need not exceed about 0.2 per cent., and it can subsequently be removed by filtration through a bed of kieselguhr and, if desired, recovered by solution in acid.

#### Fat-Hydrogenation Plants.

(i.) *Agitation Systems*.—Different types of apparatus have been introduced by various designers, the essential principle in all of which is that hydrogen is admitted at the lower part of a vessel and rises through the body of mixed fatty oil and catalyst whilst the whole is kept thoroughly mixed by mechanical agitation. The stirring must be as thorough as possible, in order to provide rapid renewal of the liquid films at the surface of the solid particles and to keep the latter evenly

distributed throughout the body of the liquid. The fat is conveniently handled in units dealing with up to ten or twenty tons at a time ; the agitation is variously effected, either by a vertical rotating shaft carrying horizontal blades working against baffles,<sup>12</sup> a horizontal rotary stirrer of similar type, an inverted cone stirrer, a "Typhoon" type of stirrer, etc.

The vessel is usually cylindrical in section and fitted with closed coils, which serve either for supplying heat by steam or cooling with water. Hydrogen enters near the base and leaves at the top by an exit pipe connected with a safety valve. The concentration of nickel may vary according to circumstances from about 0.1–1 per cent. of the fat-charge, and the operation may be carried out between 120° and 200°, usually at a pressure of between 2 and 5 atmospheres of hydrogen.

The optimum temperature of hydrogenation of fats is about 170°–180°, and the action is strongly exothermic in character, so that moderation of the temperature by cooling may be necessary.

(ii.) *Circulatory Systems*.<sup>13</sup>—Here again, there are several variants of the main principle, which consists in circulating the oil and catalyst through an atmosphere of hydrogen, instead of passing the latter through the liquid. The hydrogen is admitted through the lid of the vessel, fresh gas entering only to replace that which is combined chemically with the fat. From the lower part of the vessel a pipe communicates with a pump which continuously removes oil and catalyst, and delivers the mixture through a further pipe passing into the vessel near the top, and terminating in a spray nozzle directed towards the inside of the lid.

The proportion of the catalyst is preferably kept as low as possible (e.g., 0.1–0.3 per cent. of nickel) in order to facilitate the circulation, the temperature is raised to about 170°–200° and, the gas-space having been completely filled with hydrogen, the charge

is circulated until hydrogenation has reached the desired point. The process is usually conducted under considerably higher pressures than in the agitation systems, for example, from about 8–12 atmospheres.

This method avoids the difficulties inherent at the gland of a moving-shaft, which are somewhat troublesome when dealing with oil and hydrogen at a high temperature, but necessitates the use of a closed gas system; this involves the steady accumulation of gaseous impurities, whether toxic to the catalyst or merely inert diluents. The process is thus best adapted for work with very pure gas, such as electrolytic hydrogen.

(iii.) *Continuous System*.<sup>14</sup>—The oil to be hydrogenated is admitted at the top of the closed hydrogenation vessel, and trickles down over nickel catalyst consisting of turnings activated as described above (p. 283), whilst it meets a current of hydrogen passing up through the vessel. Excess of hydrogen is collected from the top of the vessel, and hydrogenated fat collects at the bottom and is continuously removed by a seal pipe.

This process entered the field very much later than the others, but has found considerable application. The ease of regulation of the process itself and of the regeneration of the catalyst, together with the absence of moving parts or complex ancillary plants, combine to make it a very useful type of plant for relatively small fat-hardening installations.

*Separation of Catalyst from the Hydrogenated Fat*.—In the continuous system the fat will not, as a rule, carry away with it more than traces of nickel. In the other processes the catalyst is readily removed by passing the hardened fat, whilst still warm and liquid, through a filter-press. The residual catalyst usually retains appreciable quantities of fat and, unless it is to be again employed in hardening a further batch or batches of oil, it may be extracted with petrol of

similar solvent in order to recover the entrained fat. From a deactivated or spent catalyst the nickel may be recovered, after removal of the fat as described, by solution in mineral acid; it is then available for use in the preparation of fresh catalyst, so that, apart from small mechanical losses, the nickel in process may be regarded as a capital charge.

#### Properties of Hydrogenated Fats and the Course of the Hydrogenation Action.

The fatty oils differ widely in composition, and consequently the composition and properties of the hydrogenated products vary to a considerable extent. A detailed account of the products to be obtained cannot be given here, but will be found in volumes dealing with the fat industries. Some indication of the variations in question may be afforded by a comparison of the melting-points of the following oils when completely hydrogenated :—

Completely Hydrogenated.	M.p.
Coconut, palm kernel oils . . . . .	43°-45°
Fish oils, whale oil . . . . .	52°-56°
Cottonseed oil . . . . .	62°-63°
Olive oil, arachis oils . . . . .	68°-69°
Soya bean, linseed oils . . . . .	69°-71°
Castor oil . . . . .	86°-90°

For technical purposes, *e.g.*, in the edible fat, soap or candle trades, complete saturation is rarely desired, and the progress of hydrogenation is followed by determination of the setting-point or iodine absorption on small test samples, or more rapidly by determining the refractive index of the fat, which falls parallel with the degree of saturation.

For the oils chiefly used in hydrogenation (whale, fish, linseed, soya bean and cottonseed oils), the consistency and melting-points of the hardened fats are



approximately related to their degree of unsaturation (iodine absorption) as follows :—

Iodine Absorption  
of Hardened Oils.

. Consistency.

80-90	Semi-liquid thin pastes.
65-80	Soft pastes, m.p. $30^{\circ}$ - $35^{\circ}$ .
50-65	Soft tallows, m.p. $35^{\circ}$ - $45^{\circ}$ .
35-50	Hard tallows, m.p. $45^{\circ}$ - $52^{\circ}$ .
-35	Very hard tallows, m.p. $52^{\circ}$ - $55^{\circ}$ .

Two factors connected with the course of fat-hydrogenation should be briefly mentioned :—

(i.) *Selective Hydrogenation*.—If a mixture of olein with more unsaturated glycerides, such as linolein, is hydrogenated, the latter is practically entirely transformed into olein before any of this is converted, in turn, into stearin (*cf.* p. 304). Thus the olein has to wait its turn, and, in a very rough manner of speaking, it may be said that, during hydrogenation, all the highly unsaturated fats pass through a stage corresponding to that of olive oil before they proceed to complete saturation.

Two important consequences follow from the selective character of the process :—

(a) Except over a very limited range, the composition of a hardened fat of given iodine number (say 50) cannot be simulated by mixing a much less hardened with a much more hardened fat (*e.g.*, one of 90 with one of 10 iodine number). The composition of the mixture will not be the same as that of the straight hardened fat.

(b) The olein type of glyceride is a most suitable material for many purposes, such as soaps, and for edible fats (in which any tendency to rancidity is a serious objection). Unfortunately the story is not so simple as it appears, because there is not one, but a number of "oleins" or glycerides of different mono-ethylenic acids to be met with in hydrogenated fats,

and not all of these are equally suitable for industrial use.

(ii.) *Isomeric Changes During Hydrogenation.*—In a highly unsaturated glyceride, the ethylenic linkages occur at different points along the chain of carbon atoms, and so several isomeric “oleins” may result, some of which are glycerides of oleic acids which are isomeric with the ordinary oleic acid of nature, but which differ from the latter in being solid at the ordinary temperature.

Again, when the glyceride of natural liquid oleic acid is hydrogenated, isomerisation as well as saturation takes place (*cf.* Section I., p. 18) and the corresponding glycerides of elaidic acid and of other solid iso-oleic acids are produced.

The iso-oleins are objectionable in practice, not because of their higher melting-point, but for the following reasons :—

(a) The soaps of the solid oleic acids are less soluble and much less free in lathering power than sodium oleate ;

(b) The crystal structure of the solid iso-oleins differs from that of the saturated glycerides and tends to affect the consistency and appearance of edible fats in which they are present ;

(c) The crystal structures of the corresponding free iso-oleic acids are less tractable than those of palmitic and stearic acids, which are the acids normally present in candle-making material.

These difficulties are the only serious obstacles to complete replacement, if necessary, of natural solid fats by the hydrogenated products, and they can be overcome to a large extent by suitable adjustment of the fat-charges employed in the various industries. At present fat hydrogenation is capable of controlling the price and output of the harder natural fats to a very marked degree, and in due course it is to be anticipated that many specific products of useful properties will be developed from the enormous range of semi-synthetic

glyceride mixtures potentially available in hardened fats from different sources.

The general composition of the glycerides present in some of the more common hydrogenated fats has been dealt with in various papers by Hilditch<sup>15</sup> *et al.* Selectivity is not only displayed in the preferential hydrogenation of linoleic to oleic glycerides, but also in that trioleins are largely transformed into dioleo-monosaturated glycerides before the latter pass into mono-oleo-disaturated glycerides and these, finally, into completely saturated triglycerides (tristearin). Therefore it usually happens that the high-melting, completely saturated triglycerides are not formed in quantity until the unsaturation of the original oil is very much reduced. In consequence of this, the proportion of fully-saturated glycerides (palmitostearins, etc.) in, for example, a hardened whale oil is much the same as in a lard or tallow of the same iodine value (mean unsaturation).

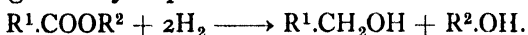
The above observations on the course of hydrogenation of a fat, and especially on the selectivity of the hydrogenation, refer to cases in which the reacting system approximates to homogeneity, *e.g.*, the "agitation" process. In the case of the continuous process where a film of oil drips by gravity downwards over the surface of a stationary mass of catalyst, movement of the oil to and from the catalyst surface is comparatively restricted and in consequence the layer of oil nearest the catalyst tends to become more completely hydrogenated than the rest.<sup>16</sup> The result is that, at the same stage of reduction of total unsaturation, a fat produced by the continuous process will contain more completely saturated glycerides and less iso-oleic derivatives, and show less selective hydrogenation of linoleic to oleic glycerides, than that produced by the agitation system.

Prejudices which have been manifested against the use of hardened fats in edible fats, soaps, etc., will die out in due course. Except for absence of vitamins,

it is established that they are in every sense hygienic and nutritious ; they are usually superior in colour, either as fat or soap, to most natural fats ; and, whilst objection could at one time be taken to a specific odour associated with soaps or fats containing hydrogenated material, it is reasonable to say that with due precaution in the hydrogenation treatment the products are almost odourless, or at most possess a very faint, not unpleasant, characteristic odour.

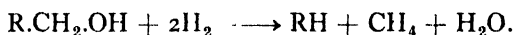
#### The Production of Higher Fatty Alcohols by Hydrogenation of Fatty Acids or Oils.

Within the last few years (about 1930), a kind of catalytic fat-hydrogenation entirely different from that discussed in the previous pages has been discovered, namely, conditions in which the carboxylic (ester) group of the fatty acid is reduced to the corresponding alcohol (or, if desired, paraffin hydrocarbon). This reaction is similar in its products to the well-known laboratory method of L. Bouveault and G. Blanc,<sup>17</sup> whereby esters are reduced by means of sodium and anhydrous alcohol to the corresponding alcohols, and may be generally expressed as follows :—



Technical catalytic processes have now been developed by means of which any natural fat, or the corresponding mixture of natural fatty acids, can be almost quantitatively converted into the corresponding normal saturated aliphatic alcohols. The process is analogous to that employed in ordinary fat hydrogenation, but the most efficient catalyst appears to be that obtained by reducing a preparation of basic copper chromate ("copper chromite catalyst"); the hydrogenation is carried out at about 200° and a pressure of 150–200 atmospheres of hydrogen. Under these conditions, any ethylenic unsaturation in the original fats or fatty acids may or may not disappear, but the acids or esters (glycerides) themselves are reduced according to the above equation.

The first patents for the use of reduced basic copper chromate as catalyst in this action were those of H. T. Böhme A.-G. and the Deutsche Hydrierwerke A.-G.,<sup>18</sup> who have developed the production of higher alcohols from fats on a manufacturing scale. The technical operations involved have been described by W. Schrauth.<sup>19</sup> The process has also been extensively investigated in the laboratory by H. Adkins<sup>20</sup> and his co-workers, who point out that it is necessary to use copper as catalyst in order to obtain high yields of alcohols. If nickel is substituted for copper, the reduction proceeds still further and, at 250° and 100–200 atmospheres pressure of hydrogen the alcohols are converted almost quantitatively into the paraffin hydrocarbons and methane :—



(On the other hand, the reduction of aryl esters appears to proceed somewhat differently and less readily. Ethyl phenylacetate for example, in presence of copper-chromium oxide at 250° and 100 atm. hydrogen, yields  $\beta$ -phenylethyl alcohol; with nickel the product is ethyl cyclohexylacetate which when treated with copper-chromium oxide and hydrogen furnishes  $\beta$ -cyclohexylethyl alcohol.<sup>21</sup> Ethyl benzoate, however, yields ethyl hexahydrobenzoate but not benzyl alcohol.<sup>22</sup>)

O. Schmidt,<sup>23</sup> contrary to Schrauth and others, maintains that the use of high pressures is not essential for the reduction of the carboxylic group, and that, in presence of reduced copper chromate, ethyl oleate is transformed into octadecyl alcohol at 270°–280° and atmospheric pressure of hydrogen. Hydrogen at pressures of 100 atmospheres and upwards is, however, most usually employed in this process, modifications of which are claimed in other patents by the I.G. Farbenindustrie A.-G.<sup>24</sup> and E. I. Du Pont de Nemours & Co.<sup>25</sup>

By this process coconut or palm kernel oil yields a

mixture of alcohols containing about 50 per cent. of dodecyl or lauryl alcohol ; tallows, lards, or palm oils similarly give a mixture of cetyl and octadecyl or oleyl alcohols ; whale oil or fish oil a mixture containing a little tetradecyl with something like equal proportions of cetyl, octadecyl, eicosyl, and docosyl and corresponding unsaturated alcohols ; and so on. The composition of the mixture of alcohols obtained from any fat naturally depends upon the proportions of the corresponding fatty acids originally present. By fractional distillation under reduced pressure the individual alcohols may be separated from each other more or less completely.

Until this very recent development in the high pressure catalytic hydrogenation of fatty acids or fatty oils it was not an easy matter to prepare a higher fatty alcohol from the corresponding acid, at all events in technical practice. These higher fatty alcohols are raw materials for the preparation of various derivatives, usually the corresponding hydrogen sulphates, the alkali salts of which are finding employment as detergents, emulsifying or wetting out agents, etc. The alkali salts of the hydrogen sulphates are in many cases stable to hard water (dissolved calcium salts) and even to dilute aqueous solutions of mineral acids.

#### Conversion of Fats into Hydrocarbons.

A certain amount of attention has been paid to the possibility of converting fats available in abundance in tropical or sub-tropical localities into hydrocarbon oils for motor fuel. A. Mailhe <sup>26</sup> showed that the red palm oil and other similar fats of West Africa can be decomposed, when heated in contact with chlorides or oxides of calcium, magnesium, zinc or tin, into hydrocarbons equal in weight to 50–65 per cent. of the original fat ; fractionation of the products should give distillates miscible with alcohol to give fuels suitable for internal-combustion engines (B. Melis <sup>27</sup>).

• The conversion of soya bean oil into fuel oil by dry

distillation of the calcium or magnesium soaps has been studied by M. Sato *et al.*,<sup>28</sup> and by S. Haga.<sup>29</sup> Sato states that the light oil (b.p.  $100^{\circ}$ – $175^{\circ}$ ) produced is readily hydrogenated by nickel at  $60^{\circ}$ – $80^{\circ}$  in the liquid phase, or at  $190^{\circ}$  in the vapour phase to a colourless oil with a pleasant odour, and that the middle oil (b.p.  $175^{\circ}$ – $300^{\circ}$ ) can be similarly hydrogenated in the liquid phase in presence of nickel. In his most recent paper (1936), Sato proposes the high-pressure "hydrogenation-cracking" of soya bean oil at or above  $430^{\circ}$  in presence of a catalyst (nickel being preferred), whereby a transparent light oil, sp. gr. below 0.7 and b.p. below  $200^{\circ}$ , can be obtained. S. Haga examined the thermal decomposition of soya bean oil in presence of active charcoal, and obtained a cracked hydrocarbon oil containing 15–23 per cent. petrol, 35–38 per cent. kerosene, and 38–47 per cent. fuel oil.

#### Hydrogenation of Benzenoid Compounds.

Liquid hydrogenation has been applied on a commercial scale to a few compounds of the benzene series, notably phenols and naphthalene. The extent of this industry does not compare with that of fat hardening, although it is growing in importance; it is, and probably will remain, more comparable with that of fine chemicals or organic "intermediates" as regards extent of output. A not unimportant factor in commercial hydrogenation of the aromatic nucleus is the consumption of hydrogen: whereas the average volume of hydrogen required per ton of fatty oil is of the order of 4,000 cubic feet, the production of one ton of cyclohexanol from phenol requires nearly 25,000 cubic feet, and that of one ton of tetrahydronaphthalene from naphthalene 12,000 cubic feet of hydrogen.

The first patents which drew general attention to the possibility of employing hydrogenation for compounds other than the fats in the liquid state were those of Br chet,<sup>30</sup> although Ipatiev's somewhat earlier

publications,<sup>31</sup> dealing with hydrogenations at what were then enormous pressures (100–150 atmospheres), pointed to the general feasibility of the process. Brochet's claims included the hydrogenation of phenols, indigo and other materials of a like character, and in general he advocated the use of about 1 per cent. of nickel at a relatively low temperature (100°–120°), and a moderately high pressure (10–15 atmospheres).

Later work has established to a certain extent specific conditions of treatment for the technical manipulation of different types of compound, and it must suffice here to give some account, by way of example, of the commercial production of cyclohexanols, hydronaphthalenes, menthol, and a few other compounds.

*Hydrogenation of Phenols.*—The commercial exploitation of reduced phenol and cresols originated in Germany under the stimulus of war conditions. The respective products from phenol and from cresols, first put on the market as hexalin and methylhexalin respectively, were found to form good emulsions with fatty soaps and to render the latter capable of holding a considerable percentage of hydrocarbon oil or tetrahydronaphthalene in homogeneous emulsion; the mixtures were found to be fairly firm in texture and their lathering power was improved rather than deteriorated. Such soaps are probably tending to replace the older naphtha or paraffin soaps.

Hexalin and methylhexalin are also useful as solvents; they have a pleasing odour, somewhat camphoraceous in type, and the odour of their esters (for example, the acetates, which also possess good solvent properties), points to some of the latter class finding application in perfumery. It may be added that a British firm markets these products under the names of sextol (cyclohexanol), sextone (cyclohexanone), etc.

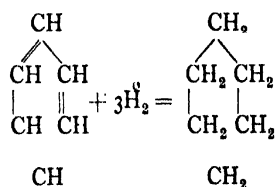
The manufacture of hydrogenated phenols may be conducted on the following general lines:—

The raw material must be freed from traces of thio-compounds and also from tarry matter, preferably by



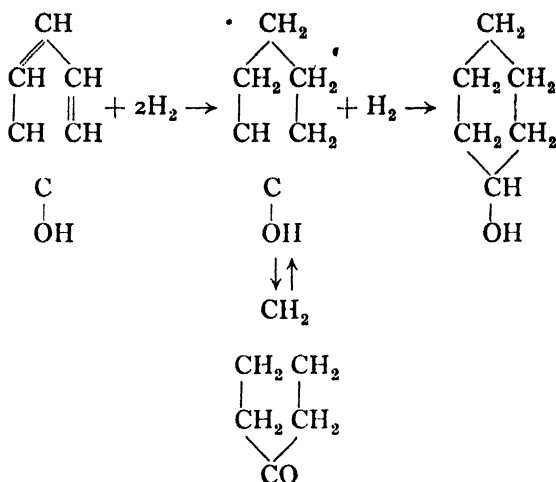
distillation in presence of a little caustic alkali. It is then placed in an apparatus of the agitation or circulatory types, together with a moderately high concentration (*e.g.*, 1 per cent. Ni) of active, and preferably supported, nickel catalyst; a carefully controlled proportion of an anhydrous mildly alkaline salt (sodium carbonate in amount equal to 25 per cent. of the metallic nickel present) may be added with advantage as a "promoter."<sup>32</sup> The reduction proceeds rapidly at 160°–200°, whilst the pressure employed may be from 4 atmospheres upwards. Obviously, the higher the working pressure the smaller will be the escape of phenol or hydrogenated phenol vapours by evaporation, but apart from this it appears that a minimum, or "threshold," pressure is necessary before catalytic reduction of the benzenoid nucleus proceeds rapidly in the liquid state.

Hydrogenation should be complete in from one to four hours, and the products may be recovered either by filtration, or by distillation from the reduction vessel, leaving the catalyst, if sufficiently active, ready for a further charge. In addition to a little unchanged phenol, the product will contain a small proportion of tetrahydrophenol or cyclohexanone derivative; the benzene ring system behaves as an individual unsaturated system during hydrogenation and, commencing with benzene itself, no dihydro- or tetrahydro-benzene is produced, but only cyclohexane:—



In the case of phenols, the action is similar, but addition of two molecules of hydrogen per molecule of phenol yields the enolic form of a cyclohexanone, and

whilst this is mainly reduced further to a cyclohexanol, some of it may remain unchanged as the ketonic compound <sup>33</sup> :—



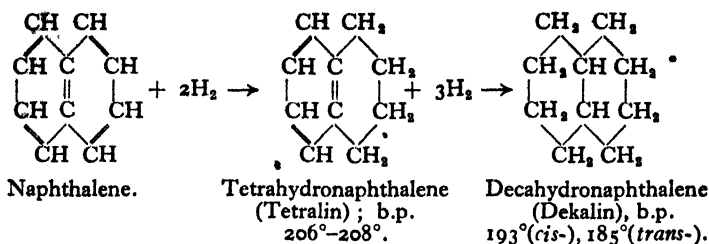
In the case of substituted phenols, two geometrically isomeric forms of the products are possible, and both are found in the hydrogenated material.

Whereas phenol melts at  $43^\circ$  and boils at  $181^\circ$ , the respective constants for cyclohexanol (hexahydrophenol) are  $25^\circ$  and  $161^\circ$ , and cyclohexanone boils at  $166^\circ$ . The six isomeric methylcyclohexanols and methylcyclohexanones are all liquids with somewhat higher boiling-points than those of cyclohexanol or cyclohexanone.

*Hydrogenation of Naphthalene.*—This has also been carried out on a fairly large scale, especially in Germany by Schroeter and the Tetralingesellschaft. The process is somewhat more difficult than in the case of phenols, because the purification of the raw naphthalene from thio-compounds demands considerable care and also because naphthalene appears to require a greater "threshold" pressure of hydrogen in order that addition of hydrogen may take place.

• Reduction takes place in two stages as follows :—

## HYDROGENATION OF NAPHTHALENE 299



Tetralin is a colourless liquid with a not unpleasant odour, and is a good solvent for many types of compounds. It is used to a notable extent as a thinner in paints and varnishes, in which it is stated to replace turpentine satisfactorily, whilst it is also serviceable as a fuel for internal combustion engines where economic considerations permit.

Dekalin, the fully hydrogenated naphthalene, has similar properties to tetralin, but the commercial hydrogenation is rarely carried to completion, since the extra consumption of hydrogen does not confer corresponding increase in the value of the product. The hydrogenated naphthalene on the market is frequently, however, a mixture of the two products in which the tetrahydro-derivative largely predominates.

The earlier patents and publications of Schroeter<sup>34</sup> and the Tetralingesellschaft<sup>35</sup> indicated that in order to obtain satisfactory hydrogenation it was desirable to refine the naphthalene by distillation over sodium, or better, by passing the naphthalene vapour through molten sodium. More recently it appears that sufficient purification results when the naphthalene is agitated with suitable qualities of fuller's earth, charcoal or kieselguhr, especially if the purified naphthalene is agitated subsequently with nickel catalyst and distilled from this into the hydrogenation vessel, which contains active catalyst suspended in tetrahydronaphthalene.

The hydrogenation may be effected in an agitator working at about 170°–200°, under a pressure of about 10–15 atmospheres; one type of apparatus described

in the literature, however, avoids the use of a mechanical stirrer, and consists of an autoclave which contains an unusually high charge of nickel on a porous or granular support. The apparatus is evacuated and a charge of purified naphthalene condensed into it after distillation from catalytic nickel, as mentioned. Hydrogen is then supplied at a pressure of 50 atmospheres or more, whilst the temperature is raised to about  $170^{\circ}$ , and absorption of the gas proceeds rapidly without stirring; when the material has been completely converted into tetrahydronaphthalene (with a minor proportion of decahydronaphthalene), the pressure is reduced to below atmospheric, and the products are distilled under vacuum and condensed.

Without exposing the contents of the hydrogenator to air, a fresh charge of purified naphthalene is distilled into the vessel and hydrogenated by means of the same catalyst, until after a number of periods of use its activity declines beyond an effective point. It has been stated that by this means the same batch of catalyst may be used for as many as 100 consecutive hydrogenations.

Naphthalene can be conveniently transformed into tetralin by passage with excess of hydrogen over stationary activated nickel in a Bolton-Lush continuous plant (cf. p. 283), at a temperature such that condensation of naphthalene on the catalyst does not take place.<sup>36</sup>

The continuous process is also used in this country for the manufacture of piperidine (or its homologues) from pyridine or methyl pyridines.<sup>37</sup> Pyridine is passed in the liquid state over activated nickel at  $180^{\circ}$  in presence of hydrogen at 20 atmospheres pressure; the products are piperidine and a little tetrahydropyridine, but no rupture of the ring-system (*i.e.*, formation of *n*-amylamine) takes place.

Tetralin and dekalin are also produced when crude naphthalene is directly treated with hydrogen in presence of molybdenum sulphide at  $300^{\circ}$ – $400^{\circ}$  and 200 atmospheres pressure (cf. Section II; Chapter IV, p. 131);

but it is not known to what extent, if any, this process has been applied to the manufacture of these substances.

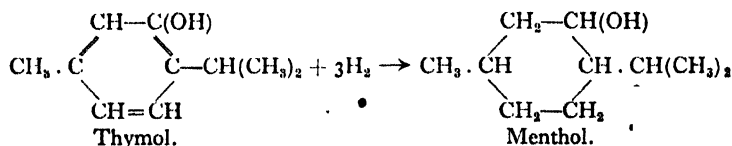
#### Hydrogenation of other Aromatic or Terpene Derivatives.

A certain number of perfumes or flavouring materials can be prepared by hydrogenation in the liquid state. Most of the unsaturated terpenes pass into saturated derivatives by this method, and in many cases the process is strongly selective, a diethylenic terpene yielding a monoethylenic compound (and frequently one only of two or more possible alternative isomerides) before any saturated derivative is produced. Relatively few of the products so far produced in the laboratory by these methods have any present value in commerce, but there is obviously considerable scope for technical research on these lines. The number of available raw materials is considerable, especially when it is remembered that aldehydic or ketonic radicals, which are also frequently present in the natural compounds, are usually reducible to alcohols by the hydrogenation process.

One instance only will be quoted here as an example of this application of liquid hydrogenation—the production of synthetic menthol.

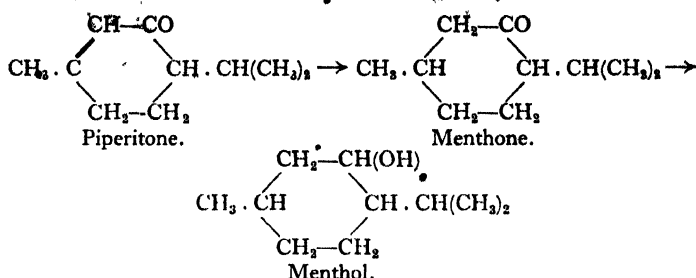
This has been effected in three ways :—

(a) From thymol by hydrogenation in a similar manner to that described in the case of other phenols (p. 296); this means has been employed to a certain extent in America :—



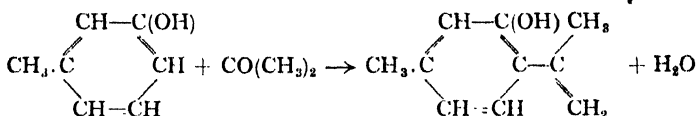
(b) From the terpene ketone piperitone, which is found abundantly in certain classes of the Australian eucalyptus (especially *E. dives* and *E. piperita*).

The course of the action in this case may be represented as follows :—



The hydrogenation proceeds readily at  $150^\circ$ – $180^\circ$  in presence of nickel under mild pressures of hydrogen (*e.g.*, 3–5 atmospheres).

(*c*) Acetone and *m*- or *p*-cresol can be condensed to yield alkylisopropenylphenols; thus, with *m*-cresol:—



The alkylisopropenylphenols, when hydrogenated, yield first the alkylisopropylphenol (*e.g.*, thymol from the condensation-product of acetone with *m*-cresol), and subsequently the corresponding cyclohexanols (*e.g.*, menthol).<sup>38</sup>

#### Notes on some other Features of Catalytic Hydrogenation in Liquid Systems.

*Small Scale (Laboratory) Hydrogenation.*—Owing to the widely extended use of catalytic hydrogenation of liquids in the laboratory, it seems desirable to refer briefly to this aspect here.

*Platinum* and *palladium* are frequently employed in the laboratory in liquid hydrogenation. Palladium is usually employed in the form of a colloidal sol, prepared by reducing an aqueous solution of palladous chloride with formaldehyde and alkali in presence of gum-arabic or similar substance, the function of which is to act as a protective colloid and retard coagulation of the palladium sol (Paal, Skita<sup>39</sup>). Colloidal platinum may be prepared similarly, but platinum black (finely

divided platinum precipitated without a protective colloid by cold reduction of aqueous platinic chloride with alkaline formaldehyde) is also quite active and somewhat more stable (Loew, Fokin, Willstätter<sup>40</sup>). Nowadays, however, catalytic platinum is usually prepared for laboratory purposes by precipitating and washing hydrated platinum oxide from the chloride; the oxide, in suspension in water, alcohol, acetic acid, etc., is readily reduced by hydrogen at atmospheric temperature and a very active form of platinum catalyst is thereby obtained. Adams<sup>41</sup> has given full details of the preparation of this form of catalyst, and of laboratory apparatus for carrying out hydrogenations, at room or slightly higher temperatures, in suitable solvents with its aid. A modified apparatus for catalytic hydrogenation on a "semi-micro-scale" has been described by Zechmeister and Chohnoky.<sup>42</sup>

*Nickel* is also used on the small scale in various forms. The Bolton-Lush continuous apparatus is available in small units about 2 in. in diameter, electrically wound for heating, and containing two cages of activated nickel turnings; the apparatus is supplied to work at atmospheric or increased pressures.

Nickel on kieselguhr or other powdered nickel catalysts can be conveniently prepared in the laboratory and used (usually at 170°–180°) either in glass or, better, steel apparatus fitted with a good stirring device. A small steel hydrogenation vessel can readily be rendered gas-tight and, with inlet and exit meters attached to measure the ingoing and emergent hydrogen, the progress of the hydrogenation of from 50 g. to about 800 g. of liquid at any temperature up to about 250° and any pressure from atmospheric up to about 5 atmospheres can be continuously followed.

A very complete study of the preparation, reduction and comparative activity of various nickel catalysts, with respect to the hydrogenation of a wide variety of compounds, was made by Adkins, Cramer and Covert.<sup>43</sup>

In the above forms, nickel is not usually markedly active below about  $120^{\circ}$  and usually reaches its optimum activity at about  $170^{\circ}$ – $180^{\circ}$  (the optimum temperature is, of course, governed to some extent by the type of compound which is hydrogenated). "Raney nickel catalyst," prepared by the action of dilute sodium hydroxide solution on nickel-aluminium or nickel-silicon, is a very finely divided, almost colloidal form of nickel which is active at temperatures down to atmospheric and which can therefore be used in the laboratory in apparatus of the type recommended by Adams and others for use with platinum or palladium (see above). Its activity is stated to be considerably accelerated by addition of a trace of platinum chloride to the hydrogenation system.<sup>44</sup> It has come into considerable prominence of late for laboratory investigations. It is conveniently prepared<sup>7</sup> for laboratory purposes, from alloys of nickel with about 50 per cent. of silicon or of aluminium, according to the directions given by Covert and Adkins,<sup>45</sup> or according to the modified procedure advised by R. Paul.<sup>46</sup> The Raney nickel catalyst is extremely sensitive to oxygen and should not be exposed to air in the dry state, but should be washed, and finally stored, under alcohol. Catalytic copper and cobalt may be produced similarly from Devarda's alloy (Cu-Al-Zn) and cobalt-aluminium alloys.<sup>47</sup>

*Selective Hydrogenation.*—The following notes may be added in general amplification of the references to this subject on pp. 289–291.

The chief investigations of selective hydrogenation of polyethenoid over monoethenoid glycerides in fat hydrogenation are those of H. K. Moore, Richter and van Arsdel,<sup>48</sup> C. W. Moore and T. P. Hilditch,<sup>49</sup> Richardson, Knuth and Milligan,<sup>50</sup> Hilditch and Vidyarthi,<sup>51</sup> Bauer and Ermann,<sup>52</sup> van der Veen,<sup>53</sup> Dhingra, Hilditch and Rhead<sup>54</sup> and H. I. Waterman and co-workers.<sup>55</sup> The main conclusions are that, in the glycerides and esters, polyethenoid (*e.g.*, linoleic)



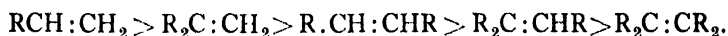
compounds are preferentially hydrogenated to the monoethenoid stage before completely saturated compounds appear in any quantity (but with the free acids the process is less selective); the selectivity is more pronounced at high than at low temperatures, and is favoured by increased concentration of catalyst in the liquid; the ethenoid groups most remote from the carboxyl group are more readily hydrogenated than those nearer, but all the ethylenic groups present in a polyethenoid molecule undergo hydrogenation to varying extents. The degree of activity of the catalyst undoubtedly affects the course of the selective hydrogenation process, and, although it is difficult to give specific references, it would appear that nickel of relatively low activity is less selective in its mode of action during fat hydrogenation than the more active forms. Dupont<sup>56</sup> states that Raney nickel catalyst, used at ordinary temperatures, renders possible selective hydrogenations which cannot be effected by the use of platinum, and also that with this catalyst acetylenic groups are reduced to the ethenoid stage before being completely saturated; with ordinary nickel catalyst this form of selectivity has not been observed. At higher temperatures ( $140^{\circ}$ – $180^{\circ}$ ) it has been generally found that the ordinary powdered nickel catalyst acts more selectively than platinum or palladium.

The progressive hydrogenation of tri- to di-, di- to mono-, and mono-unsaturated glycerides to completely saturated glycerides has already been mentioned (p. 291). All three stages proceed to some degree concurrently, but at any one contact with the catalyst only one ethenoid group in a complex triglyceride molecule appears to undergo combination with hydrogen.

The influence of mechanical conditions (as instanced by gravity flow of liquid over a stationary catalyst in the continuous apparatus), which may cause modifications in the above general statements as regards

preferential hydrogenation in cases where the system does not approach homogeneity, has also already received notice (p. 291).

Hydrogenation of an ethenoid bond is also influenced by the degree of substitution of the unsaturated carbon atoms. Lebedev and co-workers,<sup>57</sup> in particular, have shown that the order of preferential hydrogenation of substituted ethylenes is



Waterman and Vlodrop,<sup>58</sup> in common with earlier investigators, attribute selective hydrogenation of polyethenoid esters (in presence of monoethenoid compounds) to preferential adsorption of the more unsaturated molecules at the active surface of the catalyst. They have recorded the interesting observation that, in a mixture of ground-nut oil (containing both oleic and linoleic glycerides) and naphthalene at 180° and atmospheric pressure of hydrogen in presence of nickel on kieselguhr, both components are hydrogenated simultaneously.

*Hydrogenation of Organic Nitrogen Compounds in the Liquid State.*—Adkins and Diwoky<sup>59</sup> made a somewhat similar, but more exhaustive, comparison of the rate of hydrogenation of a large number of aromatic ring-systems, alone and in the form of binary mixtures. The rates of hydrogenation (at 125°–175° and 125–200 atm.) of the individual substances were in the following order: quinoline > benzene > toluene > phenol > benzyl alcohol > pyridine > diphenylamine > acetanilide > aniline. Hydrogenation of binary mixtures of these compounds showed that the order of preferential reduction was somewhat different, namely: quinoline, pyridine, aniline, benzyl alcohol, phenol, diphenylamine, benzene, acetanilide, toluene. Amino-compounds inhibited the reduction of benzene or toluene, but the presence of the latter accelerated that of aniline.

• The catalytic reduction of nitrobenzene to aniline

presents some peculiarities. Sabatier showed that, in presence of nickel at  $140^{\circ}$ – $170^{\circ}$ , hydrogen and nitrobenzene vapour yielded cyclohexylamine as well as aniline, but that, with copper at about  $250^{\circ}$ – $300^{\circ}$ , aniline was produced in good yield with no reduction of the benzene nucleus. The vapour-phase reduction of nitrobenzene to aniline in presence of copper at about  $300^{\circ}$  goes quite smoothly on a large scale with either hydrogen or carbon monoxide as reducing agent, so that purified water-gas can be substituted for hydrogen; but in this instance catalytic reduction has shown no economic advantage over the cheap and very efficient technical method which is universally employed, *i.e.*, reduction of nitrobenzene with scrap iron in presence of a little hydrochloric acid.

In the liquid phase, catalytic reduction of nitrobenzene to aniline proceeds under atmospheric pressure of hydrogen with some difficulty. S. J. Green,<sup>60</sup> however, has made the remarkable observation that, during hydrogenation of a mixture of an unsaturated fatty ester (or fat) and nitrobenzene, the latter is smoothly converted into aniline while the unsaturated fatty derivative remains almost unattacked. Similar acceleration of the reduction of nitrobenzene occurs when a mixture of the latter with a high-boiling, saturated paraffin hydrocarbon is employed, but other substances, such as methyl cinnamate or tetrahydronaphthalene, have no effect. The acceleration appears to be connected with the presence of a long-chain carbon compound which, according to Green, may cause greater dispersion of the nickel catalyst in the nitrobenzene mixture.

Adkins and Winans,<sup>61</sup> and others, have recorded the hydrogenation to aniline or corresponding compounds, without difficulty, of substances such as oximes, aldimines, azo-compounds, phenylhydrazones, dihydroglyoxalines, etc., in the liquid state.



## CHAPTER XII

### THE USE OF ACTIVATED CHARCOAL AS A CATALYST

THE element carbon, when in a form in which its surface is very large in comparison with the total volume present, has the properties of a catalyst in a number of reactions, and it is probable that its applications in this direction have not been yet by any means completely explored. A distinction must be drawn in the first place between forms of charcoal which are mainly useful for decolorising purposes (in which case the essential process is mainly adsorption of compounds of relatively high molecular weight at the surface or in the capillary interstices of a porous mass of charcoal) and carbons which, whilst as a rule highly efficient decolorising agents, also possess the property of catalysing certain reactions.

For example, animal charcoal, which consists essentially of a deposit of incinerated carbon on a mass of more or less porous calcium phosphate and other inorganic salts, has considerable decolorising power (although this is of a low order compared with modern types of absorbent carbon). Nevertheless, in certain industries, especially sugar refining, in which it is desired at the same time to remove soluble inorganic salts, animal charcoal is still preferred because the soluble mineral salts are removed or transposed at the same time by the action of the calcium salts present in the charcoal.

Modern charcoals, many of which are known in commerce under specific trade names, are produced by processes which employ, as a rule, one of the following general principles:—

(a) Carbonisation (destructive distillation) of specific wood-fibres, or sawdust from specific woods, after

impregnation of the raw material with solid or liquid compounds ;

(b) Activation of the prepared charcoal by treatment with gases or vapours at high temperatures ;

(c) Combination of the carbonisation of impregnated wood (a) with activation by gases (b).

Wood-charcoal is the most usual form, but other materials such as peat, lignite, lampblack, blood, etc., are also carbonised to yield active charcoals.

(a) *Carbonisation of Impregnated Wood Material.*—Very many inorganic compounds have been proposed as impregnating agents, including phosphoric, sulphuric and boric acids, sulphates, carbonates or sulphides of the alkali metals, ammonium, calcium and magnesium, and chlorides of zinc, iron, calcium or alkali metals. Zinc and calcium chlorides are perhaps the substances most frequently employed for the purpose.

The pyrolysis of the impregnated wood is carried on at about 800°–1,000° until volatile matter ceases to come away, the operation usually requiring several (up to about twenty-four) hours. The products are discharged into water whilst hot, and thoroughly lixiviated first with boiling water and then with hot aqueous mineral acid, and finally again with water ; the washed charcoal is dried and ground mechanically to a suitable size. Apparently the thermal decomposition of carbohydrate matter so as to produce pure carbon is an extremely difficult process. In this distillation method, in which relatively little free oxygen is available, the processes involved are mainly those of elimination of water and condensation of the cellulose decomposition products with the production of increasingly complex, difficultly volatile or non-volatile hydrocarbons. The final product is therefore, in all probability, an extremely porous material with capillary interstices approaching molecular size ; its surface, however, is not exclusively elemental carbon, but is covered to some extent by films of hydrocarbons of very high molecular weight and low hydrogen content. Such

charcoals are frequently highly active as adsorbent materials (that is, for decolorising and bleaching), but, according to Chaney<sup>1</sup> and other authorities, are not so useful catalytically as that prepared by method (b).

The "black liquor" from the soda-cellulose process, on evaporation, yields an alkali-containing residue which, when incinerated as above, gives active charcoal.<sup>2</sup>

(b) *Gas-activation of Charcoal*.—The wood or other raw material is first heated in retorts at 400°–500° until no further volatile products are evolved, after which the temperature is raised to 800°–1,000° and a current of steam, air or carbon dioxide is injected through the carbonised mass. (Chlorine, phosphorus, hydrochloric acid gas, and sulphur have also been cited as activating agents.) Steam and/or air are the gases most usually employed (*e.g.*, superheated steam mixed with 2–10 per cent. of air). The surface films of complex hydrocarbons are removed by the controlled oxidation process and, moreover, the elemental carbon surface is doubtless also partially attacked so that, in addition to the porous structure of the whole mass, the carbon walls enclosing the capillaries consist not of a smooth surface, but of what may be regarded as a lattice work of carbon atoms from which a number of the original atoms have been removed by oxidation; the carbon surface is therefore of the type which, as has been shown in Section I, p. 22, is that characteristic of an active catalyst.

The subsequent treatment of the activated product is the same as in the case of the impregnation process (a); obviously, both processes can be carried on together if desired (c). Thus, it has been stated<sup>3</sup> that an active product is obtained when powdered bituminous coal, impregnated with zinc chloride or phosphoric acid, is calcined and subsequently activated with steam at high temperatures; similarly, Chaney<sup>4</sup> has proposed to form briquettes from the raw carbonaceous material, using animal hair as binding agent;

and to carbonise the briquettes with concurrent or subsequent gas-activation.

Different authorities hold somewhat different views as to the mechanism of the activation processes, although the consensus of opinion is as suggested in the preceding paragraphs. Zerban<sup>5</sup> considers that the impregnating agents employed have, in addition to promoting condensation actions and the elimination of water from the cellulose residues, the functions of restricting the formation of films of hydrocarbons of high molecular weight at the carbon surface and of protecting the latter against oxidation. Chaney,<sup>1, 4</sup> and also M. and L. Jacqué,<sup>6</sup> attribute activation by steam or oxygen to removal of such hydrocarbon films from the capillaries of the carbon by oxidation, and also to partial, irregular oxidation of the carbon surface itself. The correctness of the latter view is borne out by the work of Garner and Blench<sup>7</sup> on the heat of adsorption of oxygen by active charcoal surfaces of this nature. It was found that the values observed were far greater than any due merely to physical condensation of the gases in the capillaries of the charcoal, and that they were intermediate between the latter values and the heat of combustion of carbon in oxygen. The order of magnitude of the thermal adsorption effects is thus quite parallel with that of a mild chemical reaction, and with those observed by H. S. Taylor and co-investigators in the case of nickel or copper and hydrogen, ethylene, carbon monoxide, etc.

More recent studies of the mechanism of formation of "active charcoal," including data as to the optimum temperature and time of heating, and the definite advantages of gas-activation of charcoal produced by the impregnation process, have been published, amongst others, by Kosakevitch and Ismailow,<sup>8</sup> and by Berl and Burkhardt.<sup>9</sup> Much still remains uncertain in our understanding of the process: for instance, there is no explanation yet forthcoming of the different



effects of metallic oxides present in the final product (lime, for example, enhancing, and ferric oxide retarding, activity). Similarly, as already hinted, there is no clear connection between catalytic and purely adsorptive powers of active charcoals. A charcoal of no great decolorising or adsorptive power may prove quite active as a catalyst or as a catalyst support, and the converse may also hold; at the same time many highly active adsorbent carbons are also excellent as catalysts or catalyst supports.

#### Main Applications of Active Charcoal as Catalyst.

These include cases of chlorination or oxidation, for example, various bleaching processes in which chlorine (or a mixture of chlorine and air) is passed upwards through a tower containing the active carbon in granular form, down which the liquid undergoing treatment is allowed to pass. Similar procedure may be applied also to the oxidation of unsaturated fatty oils of a drying nature by air. Active carbon is also effective in oxidising hydrogen sulphide or hydrogen phosphide in presence of small quantities of air, and is used to some extent in removing these impurities from industrial gases such as ammonia or acetylene.<sup>10</sup> It has also been proposed to employ active charcoal in the nitric acid absorption towers dealing with the gases from the catalytic oxidation of ammonia (*cf.* this Section, Chapter VI, p. 189); the rate of oxidation of nitric oxide to nitrogen peroxides is stated to be increased 500 times by means of active charcoal, offering possibilities of considerable reduction in the absorption-tower space compared with existing systems.<sup>11</sup>

*Phosgene* <sup>12</sup> (carbonyl chloride),  $\text{COCl}_2$ , used largely in the synthetic organic chemical industry and also in chemical warfare, and to some extent as an insecticide, was originally produced by exposing equal volumes of carbon monoxide and chlorine to bright sunlight or to ultra-violet rays, but combination has been found

to take place quite readily in the absence of light if the mixture of gases is passed through layers of activated charcoal at a moderate temperature, for example, about  $100^{\circ}$ – $125^{\circ}$ , and not above  $150^{\circ}$ . Probably all the phosgene manufactured at the present day is produced by the employment of carbon as a catalyst. So long as the carbon monoxide used is very carefully purified, the catalytic action of the active charcoal is most efficient, and one pound of the latter will suffice for the manufacture of a ton of phosgene before reactivation of the charcoal is needed.<sup>13</sup>

*Sulphuryl chloride*,  $\text{SO}_2\text{Cl}_2$ , another important reagent in the synthetic organic chemical industry, is similarly produced by combination of sulphur dioxide and chlorine in presence of active charcoal.<sup>14</sup> In this case the original procedure of passing mixtures of the gases over active charcoal appears to have been abandoned in favour of carrying out the combination in the liquid phase by suspending active charcoal in liquid sulphuryl chloride, and passing equal volumes of sulphur dioxide and chlorine into the solution. When the concentration of the catalyst falls below a certain point owing to the accumulation of sulphuryl chloride, the catalyst is separated by filtration and used again with a fresh, smaller proportion of sulphuryl chloride; the most active forms of carbon are capable of producing nearly 250 times their own weight of sulphuryl chloride per hour.

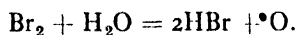
*Hydrochloric acid* is at present produced almost exclusively from the by-products of the manufacture of caustic soda by the electrolysis of brine, *i.e.*, from hydrogen and chlorine. Its manufacture forms one of the many good illustrations of fluctuations in general method which occur owing to changing economic factors and concurrent alterations in technical procedure. Originally, of course, hydrochloric acid was a by-product of the first phase of the Leblanc soda process, and in the hey-day of the latter no other source of its production was necessary. Now the

position is completely reversed, electrolytic soda is made in ever-increasing quantities, and hydrochloric acid has to be synthesised from the elemental by-products, hydrogen and chlorine.

The synthesis can be, and in fact is, effected by simply burning one gas in the other ; but in the early stages, when hydrogen was burned in an atmosphere of chlorine, the process was found to be somewhat dangerous and difficult to control without risk of explosions. This difficulty has now been overcome, the discovery having been made that by use of suitable jets and reversing the procedure, *i.e.*, burning chlorine in an atmosphere of hydrogen, the combustion can be made to proceed quite smoothly ; and this is now the chief mode of manufacture of hydrochloric acid.

In the meantime, it was found that a technically efficient and safe method consisted in passing an equimolecular mixture of hydrogen and chlorine through a bed of granular activated charcoal set in a water-jacketed vessel, the temperature of the contact mass being kept below a definite point by regulating the flow of water in the cooling system.<sup>15</sup>

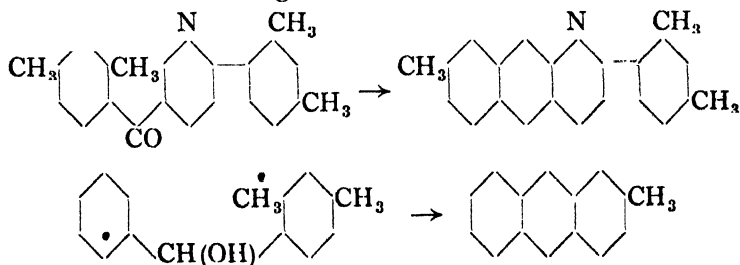
*Hydrobromic acid* <sup>16</sup> can also be prepared technically by passing a mixture of bromine vapour and steam over active charcoal at 500°, when the following action takes place :



In this process, however, the carbon is a reagent rather than, or as well as, a catalyst, since it is gradually oxidised to carbon dioxide by the oxygen liberated in the main action.

It is probable that active carbon could also be used with good effect as a chlorination catalyst in the case of many aromatic and other organic derivatives, in controlling the extent and yield of a desired product, but this does not appear yet to have been systematically studied ; the suggestion has, however, been made, to produce hexachlorethane from ethyl chloride by this means.<sup>17</sup>

*Other Catalytic Processes (Organic Compounds) with Active Charcoal as Catalyst.*—Finally, reference may be made to various recent processes which have been patented for the action of active charcoal on various types of exclusively organic chemical changes.<sup>18</sup> Thus, it has been stated that at  $300^{\circ}$ – $350^{\circ}$  active carbon converts unsaturated into saturated compounds in presence of steam, although from the details given (for example, the yield of stearic from oleic acid) it does not seem that the hydrogenating action is very vigorous. Ethyl alcohol and hydrogen chloride passed over active carbon at  $280^{\circ}$ – $300^{\circ}$  give a 75 per cent. yield of ethyl chloride, which is increased to 97 per cent. if the active charcoal contains added phosphoric acid. Other claims are for the use of active carbon in converting specific hydroxylic or ketonic aromatic compounds into polycyclic derivatives of the anthracene or quinoline types; the vapours of suitable compounds are passed, usually in presence of a certain amount of air, over active carbon at about  $400^{\circ}$ , when actions such as the following are stated to occur:



#### Active Charcoal as a support for other Catalysts.

In a number of other cases, use is made of the surface condition of activated charcoal in its employment as a support for other catalysts. In such cases the catalytic action of the charcoal itself does not, as a general rule, come into play, and the latter simply serves as a very efficient mechanical support for the specific catalyst which is necessary in the particular case. For example, nickel, platinum, palladium or

\*copper may be deposited upon active charcoal, and the products are exceedingly active hydrogenating catalysts ; such materials are not used to any great extent in industry simply because the cost of activated carbon is at present sufficiently high to restrict its application merely as a catalyst support, for many other cheaper forms of porous support yield catalysts of quite sufficient technical activity.



## SECTION III

### CATALYSIS AT SURFACES OF COLLOIDAL ORGANIC COMPOUNDS (FERMENTATION PROCESSES)

SUFFICIENT has been said in Section I., Chapters I and III, to indicate the reasons for the inclusion of some account of fermentation processes in the present book. It is, of course, out of the question to deal fully with the many ramifications of the industries connected with the production of beer, wines and spirits, although the output of alcohol in these forms is doubtless far greater than that of the whole of the other fermentation products which will be mentioned.

From the catalytic standpoint the chief interest in technical fermentation processes is their adaptation to yield specific chemical products, and discussion will be confined for the most part to such cases.

The essential difference between fermentation catalysis and ordinary catalytic action has already been defined in Section I. as the employment of a catalyst (enzyme) which is produced by a living organism, and therefore the equipment of the technologist in these industries must include not only adequate knowledge of general catalysis and of chemical transformations, but also that of mycology, bacteriology, etc. A. Chaston Chapman,<sup>1</sup> in 1919, drew attention to the fact that "as a branch of chemical industry, industrial microbiology has not received in this country the amount of attention to which its importance entitles it"; in the years which have since elapsed it cannot be claimed that a great deal has been done to remedy this defect, other than the establishment of one or two important centres of research on industrial fermentation processes. Still less is there any sign of approximation to the ideal.

of Meldola<sup>2</sup> that: "when we can transform sugar into alcohol in the laboratory at ordinary temperatures by the action of a synthesised nitrogenous organic compound; when we can convert glucose into citric acid in the same way that *Citromyces* can effect this transformation; when we can build up heptane, or cymene, or styrene, or when we can produce the naphthalene or anthracene complex in the laboratory by the interaction of organic compounds at ordinary temperatures, then may the chemist proclaim with confidence that there is no longer any mystery in vital chemistry." Nevertheless, in recent years, efficient processes for the production of glycerol, butyl alcohol and acetone from carbohydrates have been developed, and it would appear that the manufacture of lactic, citric and butyric acids from similar sources is on the eve of more scientific and efficient treatment.

Much further work is desirable on the isolation and study of specific organisms which will either give rise to higher yields than the cultures at present used, or on the other hand will lead to the production of other useful industrial chemical products. Such biochemical processes are likely to prove increasingly valuable by reducing or eliminating operating costs for fuel, power, and accessory chemicals, so long as the recovery of the products from the fermented liquor is not unduly difficult and expensive.

J. V. Eyre<sup>3</sup> considers that it seems doubtful whether any large new source of fermentable material will become available, particularly in this country, and that it is unlikely that entirely novel organisms will be discovered capable of effecting some entirely new, technically useful, change. He believes it to be more likely that advances will be chiefly made in discovering means whereby the products of known fermentation processes may be severally suppressed or increased as desired.

The examples to be dealt with in the present section include the alcoholic fermentation of sugars,\* mainly



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with reference to the variant which leads to the production of comparatively high proportions of glycerine; the acidic fermentation of sugars associated with the production of lactic, citric, or butyric acids; the biochemical oxidation of alcohol to acetic acid (vinegar); the fermentation of carbohydrates emanating from starch so as to produce butyl alcohol and acetone; the degradation of celluloses by specific types of micro-organisms; and, finally, the hydrolytic action of lipase as utilised in the hydrolysis or splitting of fats in the manufacture of fatty acids (soap) and glycerine.

## CHAPTER I

### THE ALCOHOLIC FERMENTATION OF SUGAR

THE manufacture of beers, wines and spirits is of great interest not only from its antiquity, but also from the amount of scientific study which it has received during the past hundred years ; the work of Pasteur <sup>1</sup> in France, of Hansen in Denmark, of Horace and Adrian Brown <sup>2</sup> in England, as well as that of other investigators, has done much to improve the production and enhance the quality of the numerous varieties of alcoholic beverages. Nevertheless, the main problems in these industries differ somewhat from those with which we are concerned in this book, in that the products in question are more or less dilute solutions of alcohol, whose merit depends upon their particular flavour and (to some extent) odour, this being the resultant of a particular blend of comparatively small proportions of various subsidiary materials. The maintenance of a characteristic product therefore depends largely on the type of organisms present, the variety of raw material employed, and various other factors, whereas it is desired here rather to refer to cases in which a specific organism (or rather the enzyme or enzymes produced therein) leads to the formation of definite chemical compounds in reasonably large yields.

So far as alcoholic fermentation is concerned, therefore, we need only perhaps consider the manner in which a sugar is transformed into ethyl alcohol (so far as this is at present understood), together with a few points concerning the production of industrial (*i.e.*, highly concentrated) alcohol by fermentation.

Dealing with the latter first, it is of course common

knowledge that in practically all cases yeast is employed as the means of fermenting cane sugar. Yeasts are minute plants belonging to the genus *Saccharomycetes*, of which there are very many species and varieties; many of these, especially the wild yeasts, are by no means so efficient in producing alcohol as certain cultivated forms, although they tend to multiply at a faster rate than the latter, and consequently require careful exclusion from the commercial yeast cultures. The ordinary brewer's yeast is one or other variety of *S. cerevisiæ*, whilst a few other species are also cultivated for the production of specific types of beverage, e.g., *S. ellipsoideus*.

So far as supplies of industrial alcohol are concerned, this commodity is largely produced in conjunction with the yeast industry; that is to say, the cultivation of bakers' yeast designed for employment in bread-making, etc. The conditions favouring the rapid growth of yeast are not quite the same as those obtaining in the manufacture of definite kinds of alcoholic liquor, but on the other hand active growth is accompanied by a comparatively vigorous fermentation, the dilution of the sugar (molasses) solution and the temperature of fermentation being on the whole somewhat lower than in many cases where the yeast is being used solely as a fermenting agent. After the yeast has been separated by filtration from the mash in which it has been grown, the dilute alcoholic solution is submitted to fractional distillation.

J. V. Eyre,<sup>3</sup> in his Streatfeild Memorial lecture of 1931, stated that the chief advances in the production of industrial alcohol have been in combating the development of fermentation due to foreign organisms in the mash; in employing pure culture yeast specially adapted for use in wort of high concentration; in supplying adequate nutritive materials (phosphate and nitrogen) to the fermenting mash and in keeping the latter at a suitable degree of acidity to check the development of infection; and in the addition of a definite

charge of pure culture yeast to the wort when the latter has been brought to the correct temperature. He pointed out that such refinements, at first considered trifling since they might only involve an increase of perhaps 0.1 per cent. of proof spirit per cwt. of molasses taken, actually represented a weekly gain of some 1,000 gallons of proof spirit on the basis of 500 tons of molasses fermented per week.

One of the first forms of more or less scientific fractionation stills for alcohol manufacture was that designed by Coffey; this was a pot still dealing with successive batches of the alcohol solution. Subsequently continuous stills were introduced: the theory of the working of the plate fractionation column has since been given by Soret and others, so that at the present time it is possible to design a continuous fractionating column for alcohol which will operate with practically theoretical recovery of the alcohol and at a very high heat efficiency. Different types of continuous alcohol stills are associated with the names of such firms as Blair, Campbell and McLean, or Barbet et Cie, the main principle of which is that the dilute alcohol liquor is introduced into the lower part of a large plate fractionating column, at the base of which a regulated current of steam is admitted; the alcoholic liquor is usually pre-heated, by means of heat interchangers, with some of the hot vapours from a higher point in the system. Eventually at the top of the column the vapours pass into a condenser (or two condensers in series), the condensate from which is partially returned to the top plate of the column as a reflux, whilst the remainder is drawn off in the form, usually, of about 92 per cent. alcohol. It is possible, by increasing the number of plates, to increase the concentration of the alcohol produced to 96 per cent.; but, in view of the vapour-pressure curve for mixtures of alcohol and water, it is not possible by simple fractional distillation to obtain alcohol containing less than 4 per cent. of water.

Industrial alcohol is now used not only in manufacturing chemical operations of many kinds, but is becoming increasingly important for incorporation with petrol in motor fuels. This has already developed to a considerable extent, especially in Germany and the United States, and the use of "power alcohol" will doubtless grow rapidly. In Germany admixture of ethyl or methyl alcohol with petrol is compulsory in motor fuels, and the fermentation of beet, potatoes, etc., is being rapidly extended to meet this demand. It was estimated<sup>4</sup> that in 1936 about 36,000,000 gallons of power alcohol would be used, 60 per cent. of the total production of alcohol in Germany being for this purpose; official returns indicate<sup>5</sup> that, in the first six months of 1936, 23,400,000 gallons of ethyl alcohol and 2,700,000 gallons of methyl alcohol were used in the production of "blended" motor spirit. In the United States, alcohol-petrol blends containing 5-25 per cent. of ethyl alcohol are most commonly used. It has been stated that, apart from provision of adequate acreage of suitable crops, no technical obstacles stand in the way of a large power alcohol development, and that this may be expected to take place rapidly. The first power alcohol plant was erected in 1936 in Kansas, with a daily capacity of 10,000 gallons of alcohol, to be produced from maize, potatoes and artichokes at a cost (duty free) of 25 cents per gallon.<sup>6</sup> In the United Kingdom the production of power alcohol is increasing steadily, although the total amount used is not so large as in the preceding cases; in the first quarter of each of the years 1934, 1935, 1936, the quantity of alcohol released for power purposes was respectively 260,000, 340,000 and 420,000 proof gallons.<sup>7</sup> In the Irish Free State it is hoped to produce 1,000,000 gallons of industrial alcohol per annum in five plants, the first of which was opened in 1936.<sup>8</sup> The use of power alcohol in internal combustion engines is specially suitable in hot climates, as the engine runs at a lower temperature than when petrol

alone is used ; and interest in it is therefore shown in many tropical countries.<sup>9</sup>

We will next consider some modern views as to the mechanism of alcoholic fermentation, with particular reference to their bearing on means of modifying this process so as to yield products other than alcohol. In his classical investigations on fermentation, Pasteur drew attention to the constant presence of small quantities of glycerine and succinic acid in the products of fermentation of grape sugar ; glycerine is normally found to the extent of about 3 per cent. of the total sugar fermented. Whilst the succinic acid is at present considered to be derived from the fermentation of small amounts of amino-acids, the glycerine originates directly from the sugar.

Before discussing suggested explanations of the mechanism of glucose fermentation, it should be made quite clear that fermentation of carbohydrates to alcohol, etc., is a sequence of chemical actions in which enzymes of different specific characters and properties play essential parts. If, for a moment, we go back a step further than the sugar stage and consider the analogous fermentation of starch, we find that yeast is not so readily capable of fermenting starch as, for example, enzymes of malt. The hydrolysis of starch to disaccharides (maltose) is effected by a specific enzyme diastase (or, in modern nomenclature, malt amylase). Again, the further hydrolysis of the disaccharide to monosaccharides (glucose and fructose) results from the action of other enzymes. Thus maltose is only fermented by certain yeasts containing the enzyme maltase, which is able to convert this disaccharide into two molecules of glucose ; whilst cane sugar is resolved into glucose and fructose by the action of the enzyme invertase, which is widely distributed in the vegetable kingdom in moulds, and also in many insects and animals and in most, but not in all, species of yeast. The conversion of the starch molecule into disaccharide

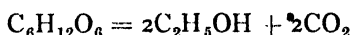
and of the latter into monosaccharide, whilst involving complex molecules, is nevertheless chemically a simple change, consisting as it does simply in the addition of the elements of water ; the necessity for employing different enzymes in different cases is simply a consequence of the fact that (as mentioned in Section I., Chapter III) enzyme and substrate have to be closely related in configuration before they are compatible.

Although we are dealing with a much simpler molecule when we come to the fermentation of a monosaccharide or hexose sugar, the stages involved in the chemical change which is usually summed up as

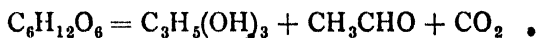


are far more drastic and complicated than simple actions of hydrolysis. Neuberg and his co-workers<sup>10</sup> showed that the fermentation of glucose takes place in three distinct ways, depending upon whether the fermenting solution (i.) is faintly acid, (ii.) contains specific salts (sulphites) capable of fixing any acetaldehyde produced or (iii.) is faintly alkaline, when a "dismutation" process occurs, whereby two molecules of acetaldehyde yield one molecule each of alcohol and of acetic acid, instead of two molecules of alcohol :—

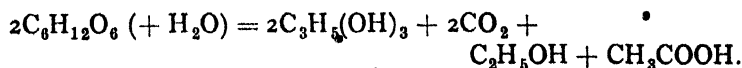
(i.) Normal fermentation in faintly acid solution.



(ii.) Fermentation in presence of sulphite or other compound capable of fixing acetaldehyde by condensation.



(iii.) Fermentation under feebly alkaline conditions ("dismutation").

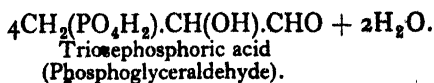
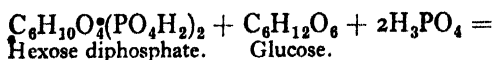


As will be shown below (in discussing the production of glycerine from sugar by fermentation) both the

second and third of these types can be realised in technical practice.

Neuberg formulated the whole process of hexose fermentation as the preliminary resolution of glucose into two molecules of methyl glyoxal,  $\text{CH}_3\text{CO}\cdot\text{CHO}$ , which, by further interaction with the elements of water, yield glycerol and pyruvic acid. The latter,  $\text{CH}_3\text{CO}\cdot\text{COOH}$ , is converted by a specific enzyme, carboxylase, into acetaldehyde and carbon dioxide. Then, interaction of a molecule each of acetaldehyde, methyl glyoxal and water was assumed to yield a molecule of alcohol and to regenerate a molecule of pyruvic acid. Acetaldehyde and glycerol, on this mechanism, are transitory intermediate products during normal fermentation; but if the acetaldehyde is fixed (as bisulphite compound) or "dismuted" (by alkali), the sequence of reactions is interrupted, and pyruvic acid is then only formed by the original "dismutation" of methyl glyoxal. Consequently, glycerol should then be produced continuously and equimolecularly with pyruvic acid or acetaldehyde.

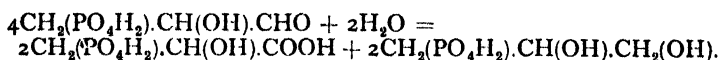
The work of G. Embden <sup>11</sup> and of O. Meyerhof <sup>12</sup> has led to much fuller understanding of the intermediate stages of the fermentation process, and has shown that, whilst pyruvic acid, as suggested by Neuberg, occupies a pivotal position in the sequence of reactions leading to acetaldehyde and then to alcohol, the prior formation of methyl glyoxal does not occur. Instead, the initial phase of the hexose transformation consists in the interaction of hexose diphosphate with glucose and two molecules of phosphoric acid, producing four molecules of a triosephosphoric acid:—



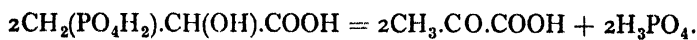
Studying the products of carbohydrate breakdown in muscle, Embden <sup>11</sup> and his co-workers showed in



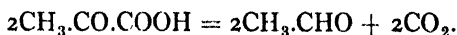
1933 that a phosphoglyceric acid or glyceric acid-monophosphoric acid,  $(\text{PO}_4\text{H}_2).\text{CH}_2.\text{CH}(\text{OH}).\text{COOH}$ , was present, whilst concurrently<sup>12</sup> in Meyerhof's laboratory the presence in the same process of *l*- $\alpha$ -glycerophosphoric acid,  $(\text{PO}_4\text{H}_2).\text{CH}_2.\text{CH}(\text{OH}).\text{CH}_2(\text{OH})$ , was demonstrated. The initial stages of the decomposition of glucose, either in muscle metabolism or during fermentation by yeast, are therefore now regarded as the production of triosephosphoric acid and the resolution of the latter into equimolecular proportions of phosphoglyceric acid and glycerophosphoric acid :—



The next stage is the production of pyruvic acid from phosphoglyceric acid :—



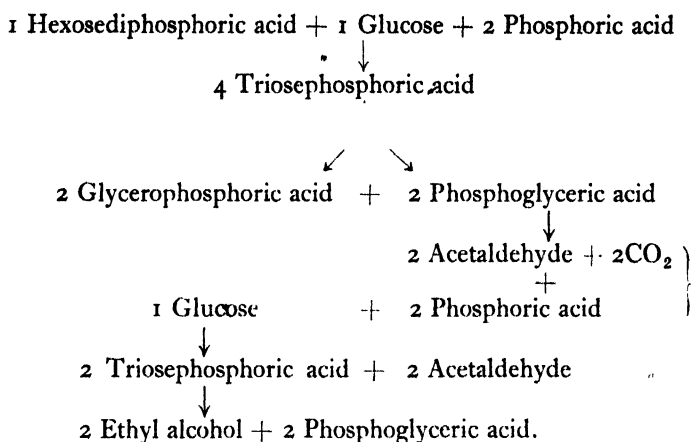
In muscle, pyruvic acid is mainly converted into lactic acid, but in presence of yeast-carboxylase it is transformed into acetaldehyde :—



It is then assumed that, in yeast fermentation under normal conditions (*i.e.*, when the acetaldehyde is not fixed by sulphites or “dismuted” to alcohol and acetic acid by mild alkali), the acetaldehyde reacts at once with another molecule of triosephosphoric acid, when the elements of water are added and a molecule each of ethyl alcohol and of phosphoglyceric acid is formed ; the phosphoglyceric acid, of course, re-enters the cycle of processes by decomposing into pyruvic acid and phosphoric acid.



The Embden-Meyerhof explanation of yeast fermentation can be summarised in the following scheme :



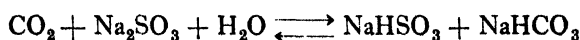
In addition to the isolation of the glycerophosphoric acid and phosphoglyceric acid, this explanation rests on much experimental evidence which cannot be detailed here, and which includes studies of the behaviour of these two compounds when added to fermenting systems, and also experimental proof of the presence and function of pyruvic acid and acetaldehyde in the fermentation process.

#### The Technical Production of Glycerine by Fermentation of Sugar.

The second or third types in Neuberg's scheme of sugar fermentation (p. 329) were first applied in technical practice during the war of 1914-1918, when the Central Powers were suffering from shortage of imported fatty materials. A process was worked out by Connstein and Lüdecke,<sup>13</sup> of the Vereinigte Chemische Werke, who found that it was possible to ferment yeast in presence of considerable proportions of sodium sulphite, and that a technical yield of 20-25 per cent. of glycerine on the sugar consumed could be obtained. The output of glycerine from beet sugar by this process in Germany and Austria

reached as much as 800–1,000 tons per month at one period of the war. Towards the end of the war Eoff, Linder and Beyer<sup>14</sup> in America studied the similar fermentation in presence of dilute alkali solution (sodium carbonate or phosphate), and found that satisfactory yields of glycerine were also obtainable by this method. So far as the present application of the process is concerned, it is stated that a large plant for the production of glycerine from sugar is in operation in the United States, but elsewhere it does not seem that at the moment the method is being widely used. At the present time the supply of glycerine from fats, hydrolysed for use in the soap or other industries, appears ample for the demands of the market; but it may certainly be affirmed that in the event of any undue shortage of glycerine from fatty sources (with consequent rise in price), the sugar fermentation process is likely to prove an effective controlling factor.

In the German sulphite process, a 10 per cent. solution of glucose or cane sugar (molasses), containing neutral sodium sulphite equal in amount (as anhydrous salt) to 40 per cent. of the sugar present, is fermented in the usual plant with ordinary brewer's yeast (*S. cerevisiae*). The action is slower than under ordinary conditions, and requires about forty-eight to sixty hours at 30° for completion. The carbon dioxide formed at first interacts with the sodium sulphite to form an equilibrium mixture of sulphite, bisulphite, and bicarbonate:—



When equilibrium is attained (neutral sulphite still being present), the remainder of the carbon dioxide is evolved in the gaseous state.

The yeast can be filtered and used again, providing that intermediately it is employed in a normal fermentation under feebly acid conditions; fresh yeast is then obtained by reproduction of the yeast cells, whereas

during the sulphite or alkaline fermentations no yeast growth takes place.

The filtered mash is treated with lime and calcium chloride in order to remove the sulphite and carbonate present, and is preferably further clarified with a coagulant such as basic lead acetate, alumina ferric, or charcoal, in order to remove the somewhat abundant non-volatile and hydroxylated by-products.

The clarified liquor is first of all distilled in a fractionating column in order to recover the aldehyde and alcohol produced; the residue from this distillation is then concentrated to crude glycerine, which is distilled for the production of dynamite glycerine by the customary methods. A thousand parts of sugar are stated to yield 230–250 parts of dynamite glycerine, 240–270 parts of alcohol, and 95–100 parts of acetaldehyde; it is also claimed that starting from crude molasses, sufficient alcohol and aldehyde can be obtained to cover the working costs of the process, leaving the value of the glycerine as clear profit.

The alternative American method is carried out somewhat similarly to the sulphite process, but it is recommended that a special variety of yeast, *S. ellipsoideus* var. *Steinberg*, should be employed, and the alkaline salt is added gradually. Thus, a 17 per cent. sugar solution may be fermented at about 30° with the yeast, sodium carbonate equal to 1.25 per cent. of the weight of sugar present being added, and further additions of the carbonate being made as the fermentation increases in rapidity, until the total amount added is equal to 5 per cent. of the original sugar; small quantities of ammonium chloride, potassium phosphate, and magnesium sulphate are also added as nutrients for the yeast. The fermentation requires four or five days for completion, and the mash is then filtered, boiled with lime and also coagulating agents, and worked up as in the case of the sulphite liquor.

No acetaldehyde is produced by this process, but the discoverers state that a yield of 20–25 per cent.

of glycerine is produced, about half of which is recoverable as dynamite glycerine. The yield of alcohol is about 30 per cent. of the sugar consumed. The amount of non-volatile organic matter present in the fermented product is somewhat larger than in the case of the sulphite method, namely, about 20-25 per cent. by carbonate fermentation as against about 15-18 per cent. by sulphite fermentation.

## CHAPTER II

### THE PRODUCTION OF CERTAIN ACIDS FROM SUGARS BY FERMENTATION

THE chief characteristics of the action of yeast on sugars have been described above, and these may be contrasted with the action of the enzymes present in many species of fungi (moulds), and of bacteria. Both of the latter classes of organisms contain many members which convert the common sugars into alcohol, usually along with other products ; but in some cases the fermentation proceeds on quite different lines and gives rise to products, some of which are dealt with in subsequent chapters, whilst others, now to be considered, include a number of acids, notably lactic, butyric, citric, fumaric and oxalic acids.

From the technical point of view, the manufacture of lactic and butyric acids is almost exclusively conducted by the fermentation processes ; that of citric acid from lemon juice, etc., is being supplemented by its production from sugar by controlled fermentation in presence of specific mould cultures, whilst it should be possible, were there any demand for fumaric acid, to produce this by means of a modified citric acid fermentation.

Lactic acid is somewhat important industrially. Various lactates are used to a considerable extent as mordants in dyeing cotton and wool, and also in calico printing, whilst the acid itself is required in large quantities in the leather industries in preparing the skins after liming and prior to the actual tanning ; it is also used, of course, in a pure form in pharmacy to some extent. Recently, certain esters of lactic acid have come into demand as solvents in the modern

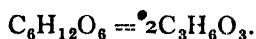
lacquer industry, and also find some application as fixatives for perfumes.

Butyric acid has not up to the present been in such wide demand, although some of its esters have a restricted use in the blending of a few perfumes and flavouring materials. There is, however, some likelihood that outlets for this acid in other directions may develop in the near future, and an efficient process for its manufacture would probably be welcomed.

The chief use of citric acid is as a flavouring material and acidulant, whilst, like lactic acid, its esters are increasingly used as fixatives in the perfume and similar trades. The supplies of the acid from natural sources, such as lemon juice, are somewhat restricted, and the price is consequently rather high; therefore it would appear that here also there is room for a scientific application of a fermentation process.

The production of lactic and butyric acids from sugars under specific conditions has been known and applied more or less empirically for very many years, but, according to A. C. Chapman<sup>1</sup> and others who are familiar with the technology of the processes concerned, the latter are capable of much improvement by taking advantage of the modern developments in microbiology.

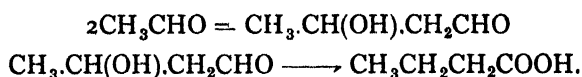
Before giving some account of the working methods used in the case of these three acids, a sketch may be given of the general nature of the chemical changes which are supposed to take place. In the case of lactic acid fermentation, the ultimate change approximates very closely to the equation:—



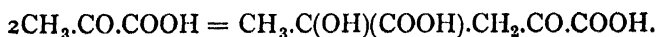
The lactic acid fermentation is one which proceeds best in presence of air, and is thus of an oxidising type.

The butyric acid fermentation, on the other hand, is anaerobic, that is to say, it proceeds in the absence of air; Buchner and Meisenheimer<sup>2</sup> suggested that its production was due to the intermediate formation of

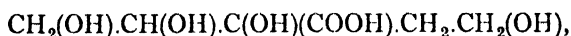
lactic acid, but it is at present supposed that the more likely mechanism is a condensation and rearrangement of acetaldehyde somewhat as follows :—



There is also some evidence <sup>3</sup> that the similar aldol of pyruvic acid (rather than acetaldehyde) may be an intermediate product in the process :—



Finally, the case of citric acid is interesting because it involves the formation of a branched carbon chain from the original straight hexose chain, a reaction which finds a parallel in the laboratory in the formation of parasaccharic acid,



from certain sugars in the presence of alkali.

*Lactic Acid Manufacture.*—Conversion of sugars into lactic acid is effected by a number of bacteria, the chief of which are several varieties of *Bacillus ateti lacti*, *B. lactis aerogenes* and *B. Delbrücki*. Most of these organisms grow very readily in milk, the casein and other nitrogenous matter of which provides particularly suitable nutrient material for the organism. In the case of sour milk, the lactic acid has been formed originally from the disaccharide lactose. The bacilli are, however, capable of attacking various sugars, including glucose, fructose, cane sugar and maltose. In the older tanning processes, the bating or deliming process was carried out by drenching the hides in an aqueous suspension of bran; this bran-drenching process owed its efficiency to the production of lactic acid, by fermentation of sugars from the starch present in the bran, that is, to the manufacture of lactic acid *in situ* in the bating process.

In the actual manufacture of lactic acid from sugar, potato starch, maize, rice starch, etc., may form the



raw material. This is subjected to diastatic fermentation in order to produce maltose or cane sugar, and the disaccharide solution (containing about 8–10 per cent. of sugar) is first sterilised by exposure to a temperature of  $95^{\circ}$ – $100^{\circ}$  for an hour. It is then transferred to the fermentation vats, where it is maintained between  $45^{\circ}$  and  $55^{\circ}$  at  $p_H$  4.5. Fermentation is started by inoculation, either with a culture from a previous fermentation, or by a fresh culture prepared from soured milk. It is necessary to have ample supplies of nitrogenous matter present as nutrient for the bacteria, either in the form of natural protein matter (e.g., bran or malt extract), or else by the use of appropriate inorganic salts, including ammonium salts, with a subsidiary amount of nitrates. Again, the organisms cannot tolerate more than about 0.5 per cent. of free lactic acid in the fermenting medium, and therefore the fermentation is conducted in presence of a suspension of chalk sufficient in amount to maintain the solution nearly neutral throughout. The fermentation should be complete in the course of from three to six days.

At the end of this time the fermented liquor (containing calcium lactate in solution) is settled and evaporated to about one-sixth of its bulk, after which it is decomposed with the theoretical amount of sulphuric acid, the precipitated calcium sulphate is removed by filtration, and the resulting solution concentrated *in vacuo* at about  $60^{\circ}$ . The commercial acid is usually sold at a strength of about 80 per cent. lactic acid.

Under good working conditions the yield of lactic acid from hexose sugar approaches the theoretical, that is to say, 100 parts of glucose will yield at least 90 parts of lactic acid: starting from starch, the yield is usually somewhat less—100 parts of maize or potato starch furnish as a rule about 70–80 per cent. of lactic acid.

**Butyric Acid Manufacture.**—As already stated, the butyric acid fermentation of sugars is essentially an

anaerobic process, and is characteristic of many of the putrefactive bacteria. Pasteur was the first to define an organism which conditions its production, and showed that the bacillus in question was present in decaying cheese, which, inoculated into a glucose solution, produced considerable proportions of butyric acid. It was subsequently found that many types of anaerobic bacteria, including those which are pathogenic to human beings and animals, induce the butyric fermentation; of those which are less markedly pathogenic the most active butyric acid producers are *Bacillus butyricus*, *B. amylobacter*, *Clostridium butyricum*, and various *Granulobacter* species.

In order to produce fermentation butyric acid on a technical scale, a solution containing up to 10 per cent. of glucose or cane sugar should be inoculated with a culture of one or other of the foregoing organisms, and fermented at about  $30^{\circ}$ – $35^{\circ}$  in vessels from which air is excluded as far as possible. Fermentation is usually complete in the course of 8–10 days, and the yield of butyric acid produced may be of the order of 30–40 per cent. In addition to butyric acid, various by-products are formed, including almost always more or less alcohol, carbon dioxide, and, as a rule, varying amounts of hydrogen, with subsidiary amounts of lactic acid, butyl alcohol, acetone, and other products. As in the case of lactic acid, the acidic products are toxic to the bacteria, and fermentation should therefore be conducted in the presence of chalk, in order to keep the solution neutral or slightly alkaline ( $p_H$  7.5–9).

The butyric acid is recovered from the fermented liquor by a preliminary distillation of the latter in order to remove volatile non-acidic products, followed by decomposition of the calcium butyrate with the correct amount of sulphuric acid, and subsequent steam-distillation and concentration of the butyric acid.

The butyric acid fermentation industry is, by com-

parison with the other processes described, in a more or less rudimentary stage, and as the demand for this product increases, the process will doubtless be overhauled and set on a more scientific basis.

*Citric Acid Fermentation.*—The production of citric acid has already been said to be conditioned by moulds; the latter contain, as a rule, a wide variety of enzymes, with the result that the decompositions induced by them are very complex and lead to many products. By suitable cultivation, however, definite moulds have been produced which have the power of converting glucose very largely into citric acid, *e.g.*, in yields of 50–80 per cent. Whilst various species of *Aspergillus* yield citric acid amongst other products, the moulds which lead to the highest yields of citric acid are species of the genus *Citromyces*, *C. citricus* (Mazé and Perrier)<sup>4</sup> being one of the most efficient. If a sugar solution containing ammonium nitrate as nutrient for the organism is inoculated with a culture of this mould and maintained at an acidity of about  $p_H$  3.5 at the ordinary temperature or somewhat higher, the formation of citric acid proceeds fairly smoothly, but slowly, to an extent approaching a 70 per cent. yield of the sugar present; as in the previous cases the acidity of the solution is best controlled by the addition of calcium carbonate.<sup>5</sup>

If the action proceeds too far, or if certain other varieties of mould, for example, *Aspergillus fumigatus*, are employed, the main product of the reaction may be fumaric acid,<sup>6</sup> and there is no doubt that the biochemical manufacture of fumaric acid could be readily achieved were there any demand for this product. Also, either form of fermentation is liable to give rise to further, more drastic decomposition with the final production of oxalic acid.

At the time of writing (1936) it appears that economic and political conditions are creating difficulties in the supply of citric acid from fruit, and that renewed interest is developing in its microbiological production.

Attention may therefore be directed to recent work by Doelger and Prescott,<sup>7</sup> Sotnikov,<sup>8</sup> Cahn,<sup>9</sup> and Quilico and Di Capua,<sup>10</sup> who have further investigated the conditions for high and uniform yields of citric acid by fermentation of sugar. Yields of 60–70 per cent. of the sugar employed can be obtained regularly in the course of a fermentation lasting about nine or ten days.

*Gluconic Acid Fermentation.*—The production of gluconic acid,  $\text{CH}_2(\text{OH})\cdot[\text{CH}(\text{OH})]_4\cdot\text{COOH}$ , from glucose by fermentation has attracted attention of late years owing to the demand for this acid for therapeutic purposes. According to Currie<sup>11</sup> and co-workers, gluconic acid can be produced continuously in 90 per cent. yield from glucose, maltose or cane-sugar by aerobic fermentation in presence of *Aspergillus niger* or *Penicillium luteum* supplied with suitable nutrient salts and in presence of an adequate supply of calcium carbonate or other neutralising agent.

## CHAPTER. III

### THE PRODUCTION OF VINEGAR BY BIOCHEMICAL OXIDATION OF ALCOHOL

THE manufacture of vinegar is, of course, practically as old as that of potable alcoholic liquors, but the scientific explanation of its formation from the latter was commenced by Pasteur from about 1860 onwards. He showed that the change was brought about by an organism to which he gave the name *Mycoderma aceti*. Later investigations by Hansen, and notably by Adrian J. Brown (1886-7), have proved that a large number of bacteria are capable of oxidising alcohol to acetic acid, and that different forms occur, one or other often predominating in specific localities or breweries, some being perhaps more rapid in action or more resistant to external conditions than others. All, however, exercise practically the same chemical function, namely, the oxidation of alcohol to acetic acid (and, subsequently, of some portion of the latter to carbon dioxide and water); but different organisms appear to some extent to tend to the formation of somewhat different by-products, which, although produced in very small proportions, confer a distinctive flavour and odour on the resulting products. The most definite of these organisms are Hansen's *Bacterium aceti*, which is commonly present in the German breweries, and Brown's *B. xylinus*, which is the main organism usually present in vinegar factories in this country.

The acetifying organisms are bacteria which, under favourable conditions, grow very rapidly and form thick, tough, gelatinous films consisting largely of a cellulose-like nitrogenous material in which the bacilli are enclosed. The organisms are relatively resistant

to both alcohol and acetic acid, and will tolerate up to 10 per cent. of alcohol, although acetifying action proceeds most readily when the alcohol concentration is below about 5 per cent. Their maximum activity is attained when the acetic acid concentration is between 2 and 3 per cent., although production of acetic acid does not cease until the concentration of the latter has reached somewhat over 6 per cent.

Bertrand found that the acetifying bacteria also have the property of converting certain polyhydric alcohols related to the sugars into the corresponding  $\alpha$ -ketoses,  $R.CO.CH_2OH$ , and referred to this type of ferment as the sorbose bacterium; thus these organisms convert glycerol into dihydroxyacetone, mannitol into fructose, sorbitol into sorbose, but are without action on certain other alcohols, such as glycol or dulcitol.

Like many other old-established industries in which efficiency had perforce to be attained by empirical methods, the vinegar industry has perhaps been somewhat slow to apply the results of the work of the bacteriologist. The procedure employed varies a good deal from one country to another, and even the raw material is not the same. Since, so far as regards catalytic action, the industry has no specific points of interest other than, for example, those which have already appeared in connection with the other acid fermentations and the ordinary alcoholic fermentation dealt with in the preceding chapters, it is only necessary here to indicate very briefly the chief features of the more important vinegar processes.

The raw materials employed as a source of vinegar may be either sugars (starch) or alcohol itself, and thus the industry may be divided into two classes, namely, the manufacture of malt vinegar and of wine vinegar.

*Malt Vinegar.*—Malt vinegar is the modern form of the industry, and has probably only been produced for a mere 300 years. Essentially this refers to the production of vinegar from beers and ales as distinct

from wines ; and in the first place, vinegar was probably made as a waste-product from ales which had turned sour, which were therefore acetified completely by addition of the "vinegar plant" (*i.e.*, the tough gelatinous film referred to earlier). Later it became the custom, which has persisted in most vinegar works, to commence the production of vinegar from malt or, in some cases, rice or maize. The preliminary fermentation of the starchy material is carried out in much the same way as in the production of beer, a diastatic fermentation being first carried out in a mash tun, whilst in some cases hydrolysis of the starch with dilute mineral acid is resorted to, followed by neutralisation with chalk.

The wort thus obtained is cooled and inoculated with yeast and fermented at a higher temperature than in the case of beer manufacture ( $22^{\circ}$ – $24^{\circ}$ ) for about three days. The object of the higher temperature is to produce more complete conversion to alcohol ("attenuation," *i.e.*, lowering of the specific gravity of the wort due to conversion of sugar into alcohol). The fermented wort, known in the trade as gyle, is frequently stored for a considerable period, when it commences to become acid and thus saves time in the actual acetification.

It should also be noted that the acetifying bacteria are themselves associated with an amylolytic enzyme, so that they can directly effect the conversion of malt starch into acetic acid. In practice, however, this is usually carried out separately as has been described. The actual biochemical oxidation of alcohol to acetic acid is carried out in vessels which are known as acetifiers, and, so far as this part of the process is concerned, the method is similar in the case of both malt and of wine vinegar ; we may therefore deal with both processes at the same time.

*Wine Vinegar.*—This is the oldest type of vinegar, and was made originally by filling oaken casks with sour wine to which a little vinegar from a previous

fermentation was added.' The casks were left on their sides in warm well-ventilated sheds kept at about 25°. The fermentation required a prolonged period for completion, and under good conditions a cask of about 100 gallons capacity would produce about twice this volume of vinegar per year.

A more rapid method for production of wine vinegar consisted in operating the process in fermentation units, consisting of two large upright open casks about 9 ft. high by 4 ft. in diameter, fitted with a perforated false bottom or tray about a foot from the base. On this perforated plate was placed a heap of beech shavings, vine-stalks or similar material, designed to expose a large surface for the support of the fungus, and also to provide a favourable medium on which it could develop fully. In carrying out a fermentation, one of the vats was completely filled, and the other only half filled with sour wine; oxidation proceeded more vigorously in the half empty cask, and at daily intervals the latter was filled up from the full cask, which was thus left half empty, and in which consequently the fermentation became accelerated.

*Modern Acetifiers.*—At a later date larger acetifiers, of similar design to those used in the malt vinegar industry, came into use. Such acetifiers have a capacity of from 3,000 gallons upwards, and consist of rectangular tanks fitted with perforated false bottoms, and packed either with shavings or basket-work as in the older system, or with a series of wooden frames so arranged that the free space between each wooden slat is only about  $\frac{1}{4}$  in. In these acetifiers the fermented wort or gyle is circulated in a fine shower from the top of the vat downwards and meets, on its downward passage over the framework or basketwork (which as usual serves as the main support for the bacteria), a current of air which is passed upwards from the base of the vessel through air holes situated below the perforated false bottom. It is essential that the total area of the air holes should be approxi-



mately the same as the area of the vents through which the spent air leaves the top of the vat. This is in order to ensure that the air on its passage upwards through the acetifier should be evenly distributed and should not give rise to channelling; it is obviously of the greatest importance to ensure that an adequate supply of oxygen is available in order to obtain the most efficient oxidation. The contents of the acetifier are maintained at a much higher temperature than in the old methods: fermentation is usually carried out at about  $40^{\circ}$  (or slightly above) in English factories (malt vinegar), and at  $30^{\circ}$ – $35^{\circ}$  for wine and spirit vinegars on the Continent. The process should be complete in twenty-four hours, and the vinegar is then ready for storage, during which a certain amount of settling and clarification occurs; after about three months' storage in vats the crude vinegar is filtered and is then ready for use.

It should be mentioned that acetification is frequently conducted in stages, as it is found that by acclimatisation the acetifying bacteria can be made more resistant to higher concentrations of acetic acid. The process is therefore usually carried out in stages in separate acetifiers in which the concentration of acetic acid is successively brought up to about 6, about 9–10, and finally to as much as 12 per cent. of acetic acid.

The latest developments in "quick" vinegar manufacture are the replacement of large acetifiers by a considerable number of comparatively small stoneware vessels, and the introduction of automatic control throughout the process. In the most modern factories there are many hundreds of these stoneware vessels, each of which is fed with the fermented wort automatically by means of a central system of pumps; the pipe system through which the liquor passes is also constructed entirely in stoneware and risk of bacterial infection is thus reduced to a minimum.

Malt vinegar is of a characteristic brown colour, and

possesses an odour due to the presence of small amounts of specific esters ; its content of acetic acid in England is usually somewhat over 4 per cent., and in Germany about 6 per cent. Wine vinegar, on the other hand, has a more definitely alcoholic odour, is pale yellow to reddish in colour, and usually contains 8-12 per cent. of acetic acid.

Other trade qualities of vinegar, such as wood vinegar or distilled white vinegar, may of course in many cases not be from a fermented source at all, but simply dilute solutions of acetic acid coloured with caramel, to which sometimes small quantities of flavouring materials may have been added.

## CHAPTER IV

### OTHER FERMENTATION INDUSTRIES BASED ON STARCH OR CELLULOSE

IN the previous chapters we have seen that sugars (or starch) can be converted into ethyl alcohol by means of yeasts, and that by suitable modification of the external conditions alcoholic fermentation can be diverted so as to produce large yields of glycerine and acetaldehyde; further, certain specific bacteria and moulds are able to transform sugars into one or other of a number of common organic acids, notably lactic, butyric and citric acids. There remain to be discussed one other very important type of sugar fermentation based on starch, and a number of instances in which cellulose material undergoes fermentation, either as such or after preliminary conversion by acids into soluble sugars.

#### The Butyl Alcohol-Acetone Fermentation of Starch.

The presence of small quantities of acetone and *n*-butyl alcohol in the products of fermentation of carbohydrates by bacterial action had been recognised for many years when Fernbach succeeded, in 1910, in producing cultures of specific bacteria which possessed the power of transforming glucose almost completely into butyl alcohol, acetone, hydrogen and carbon dioxide. Organisms of the Fernbach type are able to effect fermentation of potato starch, and the Fernbach process was in operation as early as 1912 in order to produce butyl alcohol from potato starch and so to obtain raw material for the manufacture of butadiene for a proposed commercial synthesis of rubber. In 1916, when acetone was in tremendous

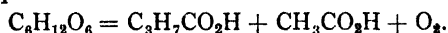
demand for cordite manufacture, work on this process was intensively revived from the point of view of production of the latter product. In the hands of Weizmann a new bacillus was isolated, which was able to effect the fermentation of starch from maize, rice and other forms of seed, such as, for example, horse-chestnuts and acorns. This process was operated, especially in Canada and the United States, on such a scale that during the later war years it became the main source of production of acetone.

The relative amounts of the organic products formed, however, are two parts of butyl alcohol to one of acetone, and in consequence huge quantities of fermentation butyl alcohol were accumulated, for which at the time there was little outlet. Subsequently the position has become reversed: the nitrocellulose lacquer industry has developed on a very large scale, and butyl alcohol is one of the most suitable media in which to apply these lacquers. Consequently this fermentation process is at present worked primarily with a view to producing *n*-butyl alcohol whilst acetone is of the nature of a by-product and is available in sufficient quantity to satisfy most of the present market demand. The later development of the fermentation process has been most vigorously carried on in the United States and Canada, but factories are also in operation in England and on the Continent.

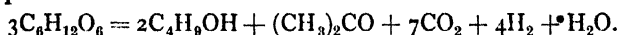
The relative merits of the Fernbach and Weizmann bacilli gave rise to considerable and somewhat heated discussions a few years ago, but it is probably a fair apportionment of credit to suggest that the original elaboration of the biochemical method leading to butyl alcohol and acetone is essentially the work of Fernbach and his collaborators at the Institut Pasteur, whilst it would appear that Weizmann succeeded in cultivating a form of organism which was somewhat more resistant than the earlier types to the fermentation conditions, and was thus able to deal with a wider variety of raw materials. Probably in present-day practice a bacillus

of the type first cultivated by Weizmann is almost always employed.

The butyl alcohol fermentation is to be regarded as a specific process, like the well-known alcoholic and lactic acid or butyric acid fermentations. The various types of bacteria which give rise to butyl or butyric fermentations are now grouped under the general name of *Clostridium butylicum*. The original forms employed were frequently species of *Gramulobacter*, whilst the Weizmann bacillus was first termed *Bacillus butylicus*, but is now usually referred to as *Clostridium acetobutylicum*. The mechanism of the action has been discussed by a number of workers, including Thaysen<sup>1</sup> and co-workers, and Speakman.<sup>2</sup> It would appear to depend essentially on the primary production of butyric acid and acetic acid from glucose, somewhat according to the equation:—



The oxygen does not appear as such, and it is probably used up in converting butyric acid or similar substances by  $\beta$ -oxidation into acetoacetic acid and hydrogen. At all events, it seems certain that the immediate sources of butyl alcohol and acetone are respectively butyric and acetic (or acetoacetic) acids. A very rough approximation to the total products yielded by the normal butyl fermentation may be given by the equation:—



The general development and mode of operation of the process may be gathered by referring to articles by Speakman<sup>2</sup> in 1919, by Killeffer<sup>3</sup> and by Woodruff<sup>4</sup> in 1927, and by Gabriel<sup>5</sup> in 1928. The first-named author gives a description of the Toronto plant which commenced operation early in 1916. This plant consisted of fourteen fermenters, 18 ft. in diameter by 20 ft. high, each holding 24,000 gallons of fermenting mash. The raw material employed was mainly maize corn, and this was prepared for fermentation by agitation with water in

mash tuns at about  $50^{\circ}$ . After shaking the necessary amount of maize meal slowly and evenly into the charge of water and heating subsequently for about 30 minutes, during which the temperature was brought to the boiling point, the mash was passed into cookers (steel tanks holding 8,000 gallons), in which it was maintained at about 10 lb. pressure of steam for over an hour in order to effect complete sterilisation. From the cookers the sterilised mash passed through a specially-designed cooler, arranged to deliver cooled mash to the fermenters at  $37.5^{\circ}$ . The fermenters were thus charged from the cookers until each contained 24,000 gallons of mash, which was then inoculated with the culture which had been prepared under laboratory conditions in an active state, and the fermentation commenced.

Bacteria are in general much more sensitive to deterioration, especially by infection with alien organisms, than the yeasts, and probably the most important point in the whole process is to destroy the microflora present in the original mash, and, after the latter has been sterilised, to cool it and ferment it under strictly sterile and aseptic conditions. In the early stages of this process, especially in the rush of war conditions, when attempts were made to transform ordinary alcohol distilleries into butyl alcohol-acetone fermentation plants, many difficulties were encountered, the majority of which were undoubtedly caused by infection.

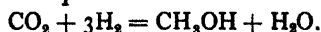
That the problems had been satisfactorily dealt with even during the war period is evident from Speakman's statement that of 3,458 charges inoculated (each consisting of 24,000 gallons of mash) between April, 1916, and November, 1918, none was rejected and not distilled.

The output of products from a plant of this type may be estimated when it is remembered that maize with a content of about 60 per cent. of starch yields 14 per cent. of butyl alcohol and 7 per cent. of acetone in commercial practice. The 1927 papers indicate that the production of butyl alcohol and acetone at that date

in America amounted to about 60 tons of butyl alcohol, 30 tons of acetone and 10 tons of accompanying alcohol per day. This involved the daily consumption of 25,000 bushels of maize corn and a corresponding production of about 6,000,000 cub. ft. per day of by-product gas, of which 2,500,000 cub. ft. was hydrogen and the remainder carbon dioxide.

The modern fermenters hold 40,000 gallons of 8 per cent. maize mash, the number of fermentations thus commenced per day being between forty and fifty. Each fermenter is inoculated with pure cultures of *Clostridium acetobutylicum*, the acidity of the mash (as in the earlier methods of operation) is maintained at  $p_H$  4.3, and fermentation is complete in 2-3 days at about  $37.5^\circ$ . The maximum evolution of gas is obtained about half-way through the fermentation, and is of the order of 8,000-10,000 cubic feet per hour. This gas in the most modern plants is passed through beds of adsorbent charcoal in order to recover small proportions of volatile organic products present therein; the daily yield from 4,000,000 cubic feet of gas amounts to over a ton of a mixture containing 55 per cent. acetone and 22.5 per cent. each of butyl and ethyl alcohols.

Suggestions are now being made to utilise the stripped gas industrially, since it consists of hydrogen in a remarkably pure condition and is suitable for catalytic purposes. It is proposed to remove the carbon dioxide by solution in water under high pressure in the ordinary way, and to use the gas for ammonia or methyl alcohol synthesis; incidentally it is stated that carbon dioxide can be used for the latter in place of carbon monoxide, according to the equation:



It has been stated<sup>6</sup> that, corresponding with the above daily production of butyl and ethyl alcohols and acetone, about 13 tons per day of methyl alcohol were synthesised in the United States, at the date mentioned, from the fermentation gases.

The preparation of the *Clostridium acetobutylicum* culture from spores is carried out with the utmost care in five successive stages, before it is put into the fermenters; cultures not more than six days old have been found best for use in plant practice. The activity of each batch of culture is carefully tested, both throughout its preparation and before use in a 40,000-gallon fermenter. The bacillus, it should have been mentioned, contains its own amylase, which effects the conversion of the maize starch into glucose, the latter then being converted, as described, into the various products.

The ferment mash (which originally contained 8 per cent. of maize starch), finally contains 2.5 per cent. of the organic solvent products and passes from the fermenters to a reservoir, from which it is pumped to continuous beer stills. These are columns 54 ft. high by 8 ft. diameter, which furnish the mixed solvent in the form of a 50 per cent. aqueous solution. This solution separates into two layers, one containing mainly butyl alcohol with some acetone, alcohol and water, whilst the other is an aqueous layer containing relatively large amounts of acetone and alcohol and relatively little butyl alcohol. Each layer is treated separately in discontinuous fractionating columns, which deliver the respective products in a state of sufficient purity for technical use.

The normal course of the butyl alcohol and acetone fermentation can be considerably modified by the addition of suitable bases or acids to the actively fermenting medium. Thus, if the increase in free acidity due to the primary conversion of sugar into butyric, acetic and other acids is prevented by continuous addition of calcium carbonate, the process can be made to furnish high yields of these acids with only minor production of the alcohols and acetone. In the other direction, the yield of acetone can be largely increased by controlled addition of acetic acid to the fermenting liquor at the stage when the produc-



tion of butyl alcohol and acetone has become rapid ; while, again, if calcium lactate, instead of acetic acid, is added at this point the yield of butyl alcohol is similarly increased.

In fact, by suitable control, the process can be made to yield either butyl alcohol, acetone, or butyric and acetic acids as its main products. It has, perhaps more than any other fermentation process, illustrated the potentialities of the biological method in industry ; and it gives rise to the feeling that there is obvious scope for the technical development of other fermentation actions, which might well lead to equally successful and important outputs of useful products.

#### Some Aspects of the Fermentation of Cellulose.

Up to the present, cellulose has not been made the starting point for the production of specific chemical compounds by direct fermentation, but the fermentation of cellulose either as such or after conversion into fermentable sugars by means of mineral acids is an important problem which concerns a number of widely differing industries.

In the first place, the conversion of cellulose into fermentable sugars has a direct bearing on the potential production of industrial alcohol, and is receiving consideration more especially from the point of view of the manufacture of alcohol as a source of motor power (*cf.* p. 327) in districts where waste cellulose (dried grass, straw, sawdust, etc.) is abundant, and in which natural supplies of oil or coal are deficient. This problem, however, is not being attacked so much by attempts at direct fermentation of cellulose as by preliminary hydrolysis of the cellulosic materials by means of aqueous mineral acids ; this treatment of cellulose will receive attention in Section IV., Chapter II, pp. 397-399, whilst the conversion of the sugars thus produced into alcohol is simply a case of the ordinary alcoholic fermentation referred to in Chapter I of this Section (pp. 324-332).

On the other hand, a certain amount of work has been carried out on the technical scale, as well as in the laboratory, on the lines of direct fermentation of cellulose, and a bacillus has been found which is capable of rapidly attacking almost every form of cellulose under either anaerobic or aerobic conditions. The most convenient source of the bacillus in question (which does not appear to be definitely classified) is steaming stable manure. It grows most rapidly at  $60^{\circ}$ – $68^{\circ}$ , but attacks cellulose steadily at any temperature between about  $35^{\circ}$  and  $70^{\circ}$ . The extraordinarily high temperature at which this bacillus reaches its maximum activity has led to its being referred to as a thermophilic organism, and in practice a temperature of  $68^{\circ}$  automatically maintains the culture in a pure condition, as the usual types of ferment are completely destroyed at this temperature.

It may be pointed out that the study of direct fermentation of resistant cellulose goes back to 1875 (Popoff) and 1883 (Hoppe-Seyler); these workers found that filter paper cellulose could be fermented with formation of methane. Omelianski<sup>7</sup> (1895–1902) and Pringsheim<sup>8</sup> (1902) extended this work and indicated that alcohol and acetic acid were also produced during cellulose fermentation. Omelianski's work was carried out at the usual temperature of about  $35^{\circ}$ , whilst Macfadyen and Blaxall<sup>9</sup> first drew attention to the action of thermophilic organisms on cellulose at about  $60^{\circ}$ , and Pringsheim<sup>8</sup> amplified this observation, noting that hydrogen, carbon dioxide, formic and acetic acids were produced at  $55^{\circ}$ – $60^{\circ}$ . In the past few years the subject has received increased attention, mainly from the point of view of power alcohol, and from the work of Langwell,<sup>10</sup> Thaysen<sup>11</sup> and others, it is to be inferred that high temperature fermentation is due to practically one form of bacillus, but that the products vary with the conditions of fermentation, including the temperature, the aerobic

or anaerobic conditions employed, etc. Langwell, working with cellulose from sulphite pulp, filter paper, cotton waste or rice-straw gives the following range of possible products :—

	Per cent.
Acetic acid . . . .	20-80
Butyric acid . . . .	0-30
Lactic acid . . . .	0-60
Alcohol . . . .	0-30
Hydrogen . . . .	0-1
Carbon dioxide . . . .	28-50
Methane . . . .	0-8

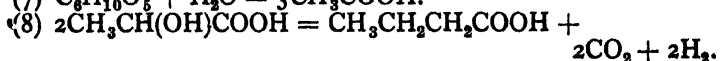
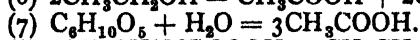
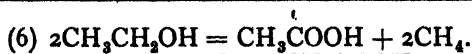
The ferment cannot tolerate more than a very limited concentration of free acetic acid ; but continuous addition of a mild alkali (*e.g.*, chalk), so that the free acidity does not exceed 0.2 per cent. (as acetic acid), permits the fermentation to proceed almost to completion. The aqueous liquor finally produced may contain 8 per cent. or more of acetic acid in the form of calcium acetate ; the acid is subsequently liberated and then concentrated by distillation (*cf.* Section IV., Chapter I, p. 386).

Free aeration appears to favour the production of ethyl alcohol, whilst with limited aeration acetic acid tends to be the main product.

Thaysen and Galloway <sup>12</sup> state that yields of 17-20 gallons of power alcohol can be obtained by fermentation of grass, straw, husks and similar waste vegetable matter.

The formation of the various products is capable of explanation, according to Langwell, on lines somewhat as follows :—

- (1)  $C_6H_{10}O_5 + H_2O = 2CH_3COCOOH + 2H_2$ .
- (2)  $CH_3COCOOH + H_2 = CH_3CH(OH)COOH$ .
- (3)  $CH_3COCOOH = CH_3CHO + CO_2$ .
- (4)  $CH_3CHO + H_2 = CH_3CH_2OH$ .
- (5)  $2CH_3CHO + H_2O = CH_3CH_2OH + CH_3COOH$ .



Thus although the problem of conversion of the complex and varied cellulose derivatives into simple products by direct fermentation is very difficult, there is reason to believe that sufficient control of the process is being reached to afford definite commercial possibilities. It should be mentioned that a not inconsiderable proportion of the celluloses (hemi-celluloses) is derived from pentose sugars, and that the latter, although not fermented by yeast, etc., are decomposed by various specific types of bacteria with production of ethyl alcohol, acetic acid, etc.

A very complete survey of work on cellulose fermentation from 1906 onwards has been contributed by Langwell.<sup>13</sup>

Apart from ultimate breakdown to simple derivatives such as alcohol, methane or acetic acid, fermentation processes play a considerable part in other industries connected with cellulose. Thus the process known as retting, usually in reference to flax and also employed with other cellulose fibres, consists in the decomposition of the pectins or gum-like components of the plant tissue which surround or are surrounded by the fibrous cellulose tissues. The pectin substances are much more readily attacked by the bacteria present in decaying vegetable matter than the cellulose fibres, and in preparing flax or other material for use in the textile industries it is subjected to a fermentation process, as a result of which the pectins are converted into soluble substances, leaving the cellulose fibres in a condition suitable for spinning, etc.

Finally, reference should be made to an important process, introduced into agriculture as the result of the bacteriological researches of Hutchinson<sup>14</sup> and his colleagues at Rothamsted. These investigators

have found that the decomposition of waste vegetable matter giving rise to the black sticky substance known as humus (which is of extreme importance in soil fertility) is effected most efficiently by a specific micro-organism, *Spirochaeta cytophaga*, of which they have isolated pure cultures. This organism acts at about 30° under aerobic conditions ; it is, however, very sensitive to the presence of organic nitrogen or of reducing sugars such as maltose or dextrose, but in presence of an adequate supply of air and of a supply of nitrogen (preferably in inorganic form) as food for the organism, together with an abundance of moisture, fermentation proceeds rapidly and in the course of a few months a heap of waste vegetable refuse is converted into a material resembling, in appearance and in nutritive value for the soil, well-rotted farmyard manure. Under the name of "Adco," a material containing suitably adjusted nitrogenous and phosphatic foods for the organism in question has been put on the market and is being used in increasing quantities by farmers and market gardeners for the purpose of converting waste vegetable material (straw, grass, leaves, etc.) into an adequate substitute for farmyard manure. The Adco process is of especial interest as an application of biochemical catalysis to one of the fundamental needs of agriculture.



## CHAPTER V

### THE HYDROLYSIS OF FATS BY MEANS OF LIPASE

THE most widely employed method of resolving natural fats into their component fatty acids and glycerine is that of the ordinary soap-pan ; the greater part of the fatty acids used in industry is required in the form of soaps and in general the ordinary soap-boiling process, consisting of direct saponification of the fat with dilute alkali by boiling in open pans, is the most satisfactory. The low concentration of glycerine in the aqueous liquor or lyes from the soap-pans is, however, a minor drawback to the efficiency of the soap-boiling process, and certainly when the fatty acids are required, as such, for soap powders or for purposes other than soap (for example, in the manufacture of candles) it becomes somewhat cumbersome to proceed by means of saponification with alkali in a dilute aqueous solution. Consequently several alternative processes have been employed, by means of which the glycerine liquors, instead of containing only 3-5 per cent. of glycerol, are obtained in the form of a 15-17 per cent. glycerine solution. One method is to carry out the fat hydrolysis in autoclaves, when the fats are hydrolysed by the action of steam at about  $120^{\circ}$ - $140^{\circ}$  in presence of a certain proportion of lime or magnesia (*cf.* Section IV., Chapter II, p. 401), whilst again, a suspension of fat in water at about  $90^{\circ}$ - $100^{\circ}$  may be hydrolysed fairly readily and smoothly by the use of a special hydrolytic agent known as the Twitchell<sup>1</sup> fat-splitting agent (see Section IV., Chapter II., p. 402).

The fatty acids produced by either of these methods are said to suffer from a tendency to assume a dark colour, but how far this is due to imperfectly under-

stood control of the processes is not quite certain ; at all events the fatty acids obtained by the lipase process about to be described are usually of very good colour, whilst the concentration of glycerine in the aqueous liquors from the process reaches as much as 16-17 per cent.

It may be mentioned in passing that the Twitchell agent, referred to above, consists of a sulphonated mixture of a fatty acid and an aromatic hydrocarbon, which has the property of emulsifying mixtures of fat and water very readily. In other words, it is almost equally attracted, so to speak, by a fatty oil and by water, and in view of what is known at the present time with reference to the orientation of fatty acids, etc., at water surfaces, it is evident that the compound in question, when distributed in a fat-water system, will arrange or orientate its molecules so that the aliphatic part of the chain is attracted towards the fat, and the acidic radicals, especially the sulphonic group, towards the water. When the fat and water are mixed in presence of the Twitchell agent, therefore, molecules of water and of fat will definitely form part of the same system (fat : Twitchell-agent : water), and in presence of the strongly acidic sulphonic group hydrolysis is effected. The Twitchell agent is thus a somewhat close artificial or synthetic reproduction of a typical hydrolytic enzyme, and the similarity to a true enzyme is reinforced by the fact that its action is reversible.

Coming to the lipase process<sup>2</sup> itself, reference should be made to the wide distribution in nature of the enzyme lipase (or, at all events, of lipoclastic enzymes). These are found in the seeds and other parts of vegetable tissue, and also in the pancreas, liver, brain, intestines, and other organs of animals. The source of the lipase used in technical fat-splitting is almost invariably castor-oil seeds, in which it is particularly abundant.

The castor-oil seeds are decorticated, carefully



separated from fragments of husk and extraneous matter, and then passed through a series of rollers, in which they are ground to a fine meal, which is intimately mixed on a perforated shaking screen with sufficient water to form a thick paste. This is centrifuged to separate the seed particles from the "seed milk" or aqueous emulsion; the latter is set aside at about  $23^{\circ}$ , and in a day or two fermentation sets in and the pasty emulsion separates into an aqueous layer and an upper layer resembling thick cream. The latter consists of an aqueous emulsion of castor-oil fatty acids holding the lipase in suspension, and is used as the hydrolytic agent.

The activity of the agent varies somewhat widely in different preparations; it has been suggested that the addition of a small proportion of sulphates of calcium or manganese to the ferment both activates and stabilises the preparation.

The fat to be hydrolysed should first be thoroughly clarified by boiling with dilute sulphuric acid, followed by settling and washing. It is then placed, together with about half its weight of water and about 7-10 per cent. of ferment cream (according to the degree of activity of the latter), in a wooden vat fitted with a perforated copper coil at the base, through which air or steam can be admitted. The charge in the vat is agitated with air through the coil until a stable emulsion results, and it is then left to stand for a day or more, during which time hydrolysis proceeds practically to completion (97-98 per cent.).

The process is best carried out in a room maintained at a temperature between  $20^{\circ}$  and  $30^{\circ}$ , this being the best range for lipase activity. The method is therefore most suited to soft oils, although tallow and hardened fats can also be handled if they are mixed with liquid fats so as to produce a semi-solid consistency at  $20^{\circ}$ - $30^{\circ}$ .

When hydrolysis is complete, the charge is agitated by means of steam in order to break up the emulsion.

as far as possible ; sometimes it is necessary to use a small amount of sulphuric acid at this point to aid in breaking the emulsion. On subsequent standing three layers are produced, the fatty acids on the top, an intermediate layer of emulsion (which manipulative technique must make as small as possible), and an aqueous layer containing the glycerine, and also a certain amount of colloidal organic matter emanating from the ferment. The clear layers are drawn off separately, and the residual emulsion is steamed with dilute sulphuric acid in order to recover more fatty acids ; whilst the clear fatty acids are washed once or twice by agitation with steam. As already stated, the colour of the fatty acids produced by this method is usually excellent.

The recovery of crude glycerine by concentration of the aqueous part of the product requires a certain amount of care, and it must be admitted that at present " fermentation crude," as it is termed, has not so good a reputation as crude glycerine produced from the autoclave or Twitchell processes of fat splitting. The lipase process has, however, not yet been employed very systematically or extensively, and it is probable that the quality of the glycerine liquor will be improved as the technique of the method is strengthened. Obviously the aqueous liquor from fermentation is always liable to contain more colloidal organic matter than in the other cases mentioned and, after preliminary neutralisation and coagulation with iron oxide or alumina in the ordinary way, it is well to pass the filtered clarified liquor through a bed of adsorbent charcoal or similar material prior to concentration. With an original fat of fair quality, a " fermentation crude " should then be obtained which, although usually dark-coloured, will not contain excessive amounts of ash and organic matter, and should be capable of distillation without serious difficulty.

The lipase process has been worked to a moderate extent in the United States and on the Continent, and

its use should extend when methods of producing the enzyme in a more stable state and less sensitive to variations in working conditions have been worked out, together with additional modifications for avoiding loss of fatty acids in the form of residual emulsion, and for reducing to a minimum the colloidal impurities which tend to pass into the aqueous glycerine layer.

## SECTION IV

### HOMOGENEOUS CATALYSIS IN LIQUID SYSTEMS

THE industrial processes which fall under this heading can be divided primarily into two classes :—

1. Those in which the chemical action involved is essentially the addition to, or withdrawal from, a compound or compounds of the elements of water.

2. A wide variety of synthetic organic reactions employed in the dyestuffs and fine chemical industries, including "condensations" in which, as a rule, water or hydrogen chloride or bromide is eliminated from two organic molecules, the introduction of halogen substituents into organic compounds, and some instances of catalytic oxidation, sulphonation, etc. These processes are exceedingly numerous, and are only illustrated in the present work by a few important examples which are typical of the rest.

The processes belonging to the first class, however, can be subdivided into three fairly well-defined groups :—

(a) *Actions of hydration, i.e.*, addition of the elements of water to one molecule, resulting in the formation of another molecular species. The fundamental technical processes with which we are concerned are :

(i.) The hydration of acetylene to acetaldehyde, and the subsequent conversion of this product (catalytically or otherwise) into a large number of synthetic aliphatic compounds of technical importance ; and

" (ii.) The hydration of ethylene to ethyl alcohol.

(b) *Actions of hydrolysis, i.e.*, addition of the elements of water to a compound with resulting formation of two independent compounds, frequently an alcohol and an acid. This important section includes the conversion of starch and cellulose into simple sugars by the

action of mineral acids, the hydrolysis of fats by the "autoclave," Twitchell and sulphuric acid hydrolysis methods, and the production of benzaldehyde and benzoic acid from benzal chloride and benzotrichloride.

(c) *Actions of dehydration*, including the removal of water from an alcohol and an acid to form an ester, the withdrawal of water from an alcohol and an aldehyde producing an acetal, and the loss of water by an alcohol leading either to an ether or an olefinic hydrocarbon.

Each of the classes mentioned forms the subject of a chapter within the present Section, while the various processes of condensation, halogenation, etc., referred to on the previous page are reviewed in Chapter IV. A fifth chapter has been added in order to collect together the chief types of polymerised organic compounds in the manufacture of which catalysts are now employed in steadily increasing numbers; the products in question include synthetic rubber, certain types of synthetic resins, lubricating oils and motor fuels.

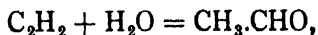
Pedantically speaking, perhaps few of these catalyses are entirely homogeneous; thus acetylene gas is passed into the liquid acid system, a gas or vapour product may result when an alcohol is dehydrated, and fats and water co-exist only as an emulsion. Yet it is tolerably certain that most of the actual catalytic changes discussed occur in a homogeneous liquid system, and for this reason they are appropriately treated in one and the same section.

## CHAPTER I

### THE INDUSTRIAL SYNTHESIS OF ALIPHATIC ORGANIC COMPOUNDS FROM ACETYLENE OR ETHYLENE

#### The Production of Acetaldehyde from Acetylene, and its Transformation into other Technically Useful Organic Compounds.

*General.*—The first patent for the catalytic hydration of acetylene into acetaldehyde appears to have been granted in 1910. Since that date, and owing especially to the stimulus of war conditions in 1915–1916, a very large industry in simple synthetic organic derivatives has been based on the fundamental interaction

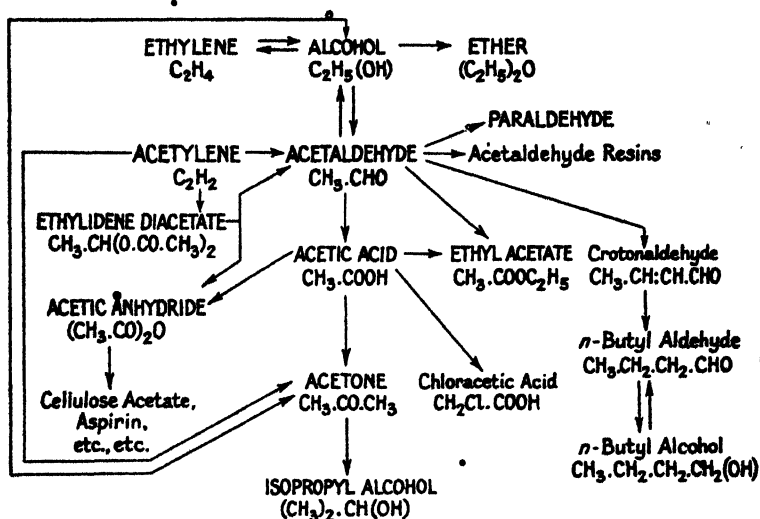


which is carried out by the catalytic hydrating action of warm dilute acid solutions of mercuric salts on acetylene.

The Chemische Fabrik Griesheim-Elektrön,<sup>1</sup> and others of the large chemical manufacturers in Germany, the Société chimique des Usines du Rhône in France, the Elektrizitätswerk Lonza and the Société de Chimie industrielle de Bâle in Switzerland, the British Cellulose and Chemical Manufacturing Co.<sup>2</sup> in England, the Carbide Industrial Co., Fredrikstad, Norway, and the Canadian Electrochemical Products Co.<sup>3</sup> of Shawinigan, have been prominent in connection with these processes. The last-named company has developed the manufacture of acetaldehyde derivatives on a commanding scale, and is probably at the present time the greatest single producer of acetic acid. In 1919 a production of about 18,000 tons of glacial acetic acid was attained; in 1935 the capacity of the plant was 48,000 tons in terms of acetic acid, and the actual production of acetic acid 36,000 tons.

## THE ACETYLENE-ALDEHYDE INDUSTRY 369

The scope of the acetylene-acetaldehyde industry can be indicated most suitably in diagrammatic form :—



Of the transformations indicated in this scheme, all but a very few are carried out by modern processes of catalysis.

The development of these industries illustrates particularly well the counterplay of economic factors in chemical industry. Synthetic acetic acid has proved a keen competitor for the old glacial acetic acid obtained from wood distillation; it can be obtained in 99 per cent. purity by a single fractional distillation of the oxidation liquor from acetaldehyde (p. 383), and, with suitable location for the manufacture of carbide, can be produced cheaply and in high yield from acetylene. On the other hand, attempts which have been made in Switzerland and elsewhere to produce industrial alcohol from acetaldehyde do not seem to

have yielded the material at rates which compete with fermentation alcohol, in spite of cheap power, acetylene and hydrogen, and of the fact that the reduction process worked efficiently.

Again, synthetic acetone from acetic acid was originally in much demand, and was indeed the first aim of the acetylene-aldehyde process; contemporaneously, however, the *Granulobacter* fermentation of starch (p. 349), yielding acetone and *n*-butyl alcohol, was developed, and fermentation acetone proved to be the more economic form of the product. Nevertheless the demand for butyl alcohol is at present much greater than that for acetone, and in consequence considerable quantities of *n*-butyl alcohol are produced from acetaldehyde by the sequence of operations indicated in the above scheme and referred to again below. Finally, in localities where alcohol or acetylene is obtainable at sufficiently low cost, acetone is still manufactured from them; not, however, by the three-stage catalytic process: alcohol or acetylene  $\rightarrow$  acetaldehyde  $\rightarrow$  acetic acid  $\rightarrow$  acetone, but by passage of alcohol or acetylene with steam over alkalisied iron catalyst at  $450^{\circ}$  as described in Section II., Chapter X, p. 261, when acetone is produced direct in about 80 per cent. yield of theory.

*The Direct Conversion of Acetylene into Acetaldehyde.*

—The method described in Matheson's English Patent<sup>4</sup> No. 132557 of 1918 may be quoted to illustrate the manner in which this process is carried out in factory practice.

The reaction vessel, a closed agitator constructed of a silicon-iron alloy and provided with a mechanical stirrer and coils for cooling or heating, is charged with 1,000 gallons of 6 per cent. sulphuric acid to which is added 25 lb. of mercuric oxide. A vigorous current of acetylene (about 60 cubic feet per minute) is passed through the liquid whilst mechanical agitation is applied. The action is exothermic, and is carried on at  $60^{\circ}$ – $65^{\circ}$ , mainly by its own heat, cooling being resorted



## THE ACETYLENE-ALDEHYDE INDUSTRY 371

to when necessary ; the system is maintained at atmospheric pressure, except for the back-pressure exerted by the exit acetylene scrubber (up to 2 lb. per square inch). The considerable excess of acetylene present carries away all the acetaldehyde produced, and passes successively through a cold-water condenser, a refrigerated condenser at  $-10^{\circ}$  to  $-15^{\circ}$ , and finally through a cold-water scrubber. The scrubbed gas is pumped back to the reaction vessel or collected in a storage holder for re-utilisation.

The aldehyde, whether condensed or dissolved in the scrubber water, is readily rectified by fractional distillation, whilst acetylene dissolved in the scrubber liquor is simultaneously recovered.

Water is removed from the reaction vessel both by chemical combination and by evaporation, and this is compensated for by continuous addition of sufficient water to maintain a constant concentration of sulphuric acid in the agitator. Mercuric oxide is also added from time to time to compensate for the slow loss of mercuric salt from the system, by reason of reduction to metallic mercury. At the temperature and acid-concentration selected, side reactions which involve reduction of mercury to the metallic state are probably at a minimum, but they cannot be completely suppressed and a sludge of mercury globules, together with minor amounts of sulphur and phosphorus compounds from the acetylene, slowly accumulates at the bottom of the vessel.

Eventually, also, non-volatile compounds from slight decomposition and polymerisation of the acetaldehyde accumulate to an unwelcome extent in the reaction liquor, which then has to be replaced by a fresh charge. This condition is only reached, however, after prolonged working, during which period the mercuric oxide has been more or less continuously added to the system and withdrawn in the form of mercury sludge.

The yield of acetaldehyde produced by this process

from acetylene is very high and probably approaches 95 per cent. of the theoretical. At the Shawinigan plant of the Canadian Electrochemical Products Company, 500,000–600,000 cubic feet of acetylene were converted per day in 1919 by this process into acetaldehyde.

The accumulated sludge of impure mercury gravitates to the bottom of the reaction vessels, whence it is periodically withdrawn and passed on, after washing and coagulating as far as possible, into a shallow iron vessel where it forms the anode of an electrolytic circuit and rests beneath a layer of 3–10 per cent. caustic soda solution. It is thus re-transformed into mercuric oxide by anodic oxidation (at a current density of 55 amperes per square foot and 8–10 volts), the product being removed as formed by a stirrer which sweeps the surface of the metallic mercury.<sup>4</sup>

In the Shawinigan process, therefore, both the raw material (acetylene) and the catalyst (mercuric oxide) are produced by electric power, which replaces all chemicals other than lime and coke for the acetylene, and the minor amount of mercury necessary to compensate for mechanical losses; thus providing a striking illustration of the efficiency afforded by cheap and abundant electricity in chemical industry.

It may be added that the earlier patents of the Chemische Fabrik, Griesheim-Elektron,<sup>1</sup> the Consortium für Elektrochemische Industrie,<sup>1</sup> and other continental firms, indicate a wide range of temperature and concentration of acid, the earliest disclosure (E.P. 29073/1910) advocating the use of 45 per cent. sulphuric acid or 25 per cent. phosphoric acid. It was observed that the higher concentrations of acid tended to retard the reduction of the mercuric salt present, but, of course, increased the loss of aldehyde due to polymerisation and resinification. Prior to the appearance of the Shawinigan patents,<sup>4</sup> the general tendency was to recommend the use of more dilute mineral acid<sup>5</sup> (or, for example, of acetic acid containing a small

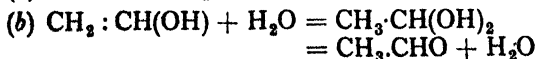
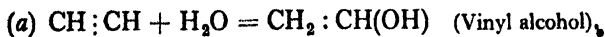
amount of sulphuric acid) coupled with a moderate temperature, *e.g.*, between  $55^{\circ}$  and  $70^{\circ}$ .

The milder mineral acid conditions conduced to higher yields of acetaldehyde and less fouling of the reaction solution with organic by-products, whilst suggestions were made to prolong the life of the mercuric salt by addition of suitable oxidants. Thus, Meister, Lucius and Brüning<sup>6</sup> observed that the presence of ferric salts or of chromic acid increased the amount of aldehyde producible by unit weight of mercuric salt, whilst Crosfield's and Hilditch<sup>7</sup> showed that periodical addition of hydrogen peroxide, peracids or peroxides, such as manganese dioxide, lead dioxide, etc., to the spent reaction liquor reconverted the mercury present to the active mercuric salt.

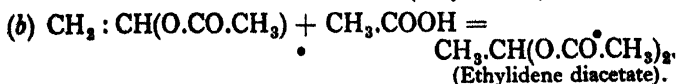
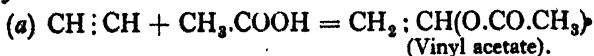
Undoubtedly, however, this process is most effectively carried out, as already stated, under conditions where a natural supply of cheap electric power is available, in place of catalyst recuperation by chemical methods.

*The Conversion of Acetylene into Ethylidene Diacetate.*  
—If glacial acetic acid is employed in place of aqueous mineral acid in the foregoing interaction, acetylation occurs in addition to, or in place of, hydration. The reactions involved may be regarded as follows :—

*Hydration—*

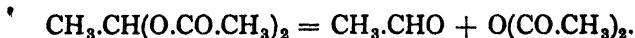


*Acetylation—*



At first sight this is a complication of the alternative synthesis of acetaldehyde, but its importance lies in the

fact that ethylidene diacetate can be readily decomposed into acetic anhydride and acetaldehyde :



This method, therefore, provides a means for producing acetic anhydride from acetic acid, whilst in the same sequence of actions acetylene is converted into acetaldehyde, which serves by oxidation to yield fresh quantities of acetic acid. Since acetic anhydride is required in large quantities, this relatively simple means of production is sufficiently attractive to make it of considerable technical importance.

Vinyl acetate has recently come into prominence because it can be polymerised into technically useful resins, and therefore the acetic acid process for hydration of acetylene is now operated so as to produce both products concurrently (see below).

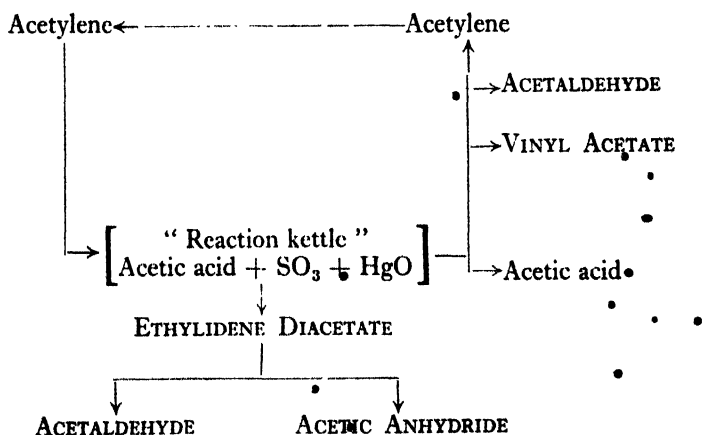
The earlier patents dealing with this reaction were mainly due to Boiteau <sup>8</sup> and the Société chimique des Usines du Rhône, <sup>9</sup> whilst later improvements <sup>10</sup> have been protected by the other large concerns operating in this field.

The technical procedure is similar to that in the conversion of acetylene into acetaldehyde, the aqueous sulphuric acid being replaced by a charge of anhydrous acetic acid, to which is added a small percentage of mercuric oxide and about 2 per cent. of sulphuric or phosphoric acid. Morrison and Shaw <sup>10</sup> have described the conditions under which either vinyl or ethylidene acetate may be made the main product of the reaction, and also the manner in which the process is usually carried out at the present time. The addition of concentrated sulphuric acid has been replaced by that of oleum or, better still, of sulphur trioxide. In the system acetic acid—2 per cent. sulphur trioxide—2 per cent. mercuric oxide, a low rate of flow of acetylene at 75°–80° leads mainly to the formation of ethylidene diacetate, while rapid flow of acetylene at 50°–60° favours the production of vinyl acetate: Sub-

stitution of ortho-phosphoric acid for sulphur trioxide is stated to promote production of vinyl acetate, while meta- or pyro-phosphoric acid tends towards formation of ethylidene diacetate.

The procedure usually followed is to operate a "reaction kettle" charged with a batch of acetic acid containing 2 per cent. of sulphur trioxide and mercuric oxide at  $50^{\circ}$ – $60^{\circ}$  with a moderate flow of acetylene, when both vinyl and ethylidene acetates are produced. The latter (b.p.  $169^{\circ}$  with decomposition) accumulates in the reaction kettle, while excess of acetylene, any acetaldehyde produced, vinyl acetate (b.p.  $73^{\circ}$ ) and small amounts of acetic acid vapour pass into a continuous fractionating column, where they are separated, the acetylene being recirculated. When the reaction slackens, the contents of the "kettle" are distilled, giving first unchanged acetic acid, then acetaldehyde and acetic anhydride from the decomposition of ethylidene diacetate; the residual sludge from the catalyst is calcined to recover the mercury, which is converted back to oxide by anodic oxidation.

The operation of the process may be represented diagrammatically as follows :—

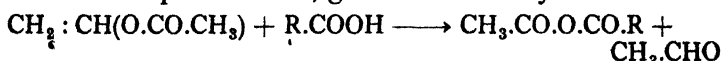


Decomposition of the ethylidene diacetate is aided

by the presence of small quantities of anhydrous salts or acids of a dehydrating nature ; zinc chloride, sodium pyrophosphate, boric acid or sulphuric acid have been proposed for this purpose. The distillation is best effected at a low pressure (*e.g.*, 100 mm.) and a temperature not exceeding about  $80^{\circ}$ , whilst it is also stated that by heating the ethylidene diacetate at about  $125^{\circ}$ – $135^{\circ}$  at atmospheric pressure in presence of acid salts, such as pyrophosphates, or with granulated zinc, almost quantitative resolution into acetaldehyde and acetic anhydride can be obtained.

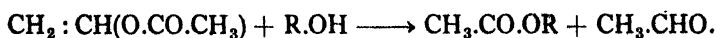
If a strong acid such as sulphuric acid is used at this stage, the acetaldehyde may be largely polymerised into paraldehyde, a derivative which is used to a considerable extent in medicine.

Vinyl acetate itself, when heated under reflux with a carboxylic acid and a little sulphuric, phosphoric or benzene-sulphonic acid, gives mixed anhydrides <sup>11</sup> :—



If acetic acid is employed, the products are acetaldehyde and acetic anhydride in about 70 per cent. yield.

With alcohols or phenols in presence of sulphuric acid, vinyl acetate similarly yields acetaldehyde and esters of acetic acid <sup>11</sup> :—



#### Products Derived from Acetaldehyde.

We will deal in the next place with materials of technical value which are produced at the present time from synthetic acetaldehyde. Whilst attention must be concentrated upon those compounds which are obtained from the aldehyde by the application of further catalytic methods, it is proposed to make the list as complete as possible, independently of whether subsequent treatment of the acetaldehyde is by catalytic means or otherwise.

Three classes of products may be distinguished :—

- (a) *Polymerised or condensation derivatives of acetalde-*

- hyde (paraldehyde, acetaldehyde resins, ethyl acetate and crotonaldehyde);
- (b) *Reduction products* (ethyl alcohol and its derivatives);
- (c) *Oxidation products* (acetic acid and its derivatives).

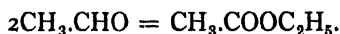
(a) *Polymerised or Condensation Derivatives of Acetaldehyde.*—*Paraldehyde* <sup>12</sup> is the trimolecular form of acetaldehyde ( $C_2H_4O$ )<sub>3</sub>, and is a liquid of characteristic odour which boils at 124°. It has an extended use in medicine as a powerful sleep-inducing and sedative agent, whilst suggestions have been put forward recently for its use, in conjunction with alcohol or petrol, as a motor fuel.

Acetaldehyde is readily transformed into the trimolecular polymeride in presence of small quantities of strong acids. Simple contact with minute amounts of concentrated hydrochloric acid causes acetaldehyde to pass into paraldehyde with considerable evolution of heat. The action is conveniently carried out by agitation of acetaldehyde, in a cooled vessel with a good condenser, with successive additions of a few drops of the concentrated acid, until further addition causes no liberation of heat. The action is an equilibrated one, and when a final state of balance is reached the mineral acid is exactly neutralised with bicarbonate (in order to avoid any aldol condensation) and the mixture is fractionally distilled, when unchanged aldehyde is first recovered and subsequently the paraldehyde which has been formed distils over.

*Acetaldehyde resins* <sup>13</sup> may next be mentioned; it has been found that acetaldehyde, as well as formaldehyde, is capable of condensation with phenols, the products being complex, difficultly-fusible or insoluble resins of a similar nature to the well-known phenol-formaldehyde or bakelite compounds. Whether such acetaldehyde resins are in every respect equally serviceable with the formaldehyde products does not appear yet to be conclusively settled, but patents have

been taken out for their production from phenols and either acetaldehyde itself or paraldehyde, usually by means of condensation in presence of a mineral acid (*cf.* this Section, Chap. IV., p. 426).

*Ethyl acetate*<sup>14</sup> (*cf.* also p. 408) can be produced directly from acetaldehyde in very high yields by what is essentially a polymerisation process :—



This action, which recalls the conversion of benzaldehyde into benzyl alcohol and benzoic acid in presence of caustic potash :



or into benzyl benzoate by means of sodium (*cf.* p. 409), is effected by means of small proportions of aluminium ethoxide (amyloxide, butyloxide). The ethoxide alone does not produce a very high conversion of aldehyde into ester, but if anhydrous aluminium chloride is also present the conversion usually exceeds 90 per cent. Another patent advises that a mixture of anhydrous aluminium chloride and aluminium powder be refluxed with alcohol and ethyl acetate until the metal present has been transformed into alcoholate with evolution of hydrogen. The resulting liquid, which contains aluminium chloroethoxides, is then well cooled and acetaldehyde is run in with vigorous stirring and cooling until, for example, the aluminium derivatives present form only about 5 per cent. or less of the whole. The aldehyde is rapidly transformed into ethyl acetate, which is purified by fractional distillation.

This polymerisation affords the most direct synthesis of ethyl acetate (which is, of course, an important solvent and fine chemical) from acetylene *via* acetaldehyde.

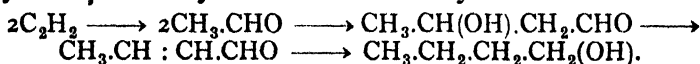
It should also be borne in mind that the process, although not at present used to this end, represents a dual synthesis of ethyl alcohol and acetic acid from



acetylene, capable of technical application if circumstances warranted the use of the method.

Ethyl acetate is stated to be produced in one operation from ethyl alcohol when the latter is heated in the liquid phase with a copper-alumina or copper-chromium oxide catalyst at  $220^{\circ}$  and high pressure, dehydrogenation being accompanied by dimerisation.<sup>15</sup> If potassium carbonate is also present in the catalyst mass the main products are *n*-butyl and *n*-hexyl alcohols.

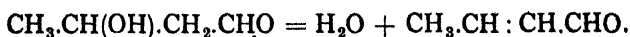
*Crotonaldehyde* represents a further type of intermolecular condensation of acetaldehyde which is of technical importance as a link in the commercial synthesis of butyl alcohol from acetylene :—



The intermediate product, aldol,  $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{CHO}$ , is produced by the action of mild alkaline agents on acetaldehyde, excess of alkali or the use of too caustic an alkali leading to the formation of large proportions of sticky, semi-solid complex aldehydic resins. It has been proposed, for example, to treat the acetaldehyde with strontium oxide, whilst baryta or lime are probably effective under controlled conditions. In modern practice, very dilute alkali (below 0.005N sodium hydroxide or about 1 per cent. of sodium carbonate) is used as condensing agent,<sup>16</sup> the temperature being kept below  $15^{\circ}$  during the condensation. An interesting proposal to assist the temperature control is to carry out the process in presence of a sufficient amount of an inert hydrated crystalline salt (*e.g.*,  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ ), when the water necessary to promote the condensation is obtained by endothermic dehydration of the hydrated crystals; this process is accompanied by absorption of heat, so that provision of water and absorption of some of the heat of condensation are simultaneously effected.

The crude condensation product, on distillation at ordinary pressure in a current of inert gas, first of all

yields unchanged acetaldehyde and then, at a somewhat higher temperature, the aldol breaks up into water and crotonaldehyde :—



It has been recommended, in order to minimise the formation of resins, to carry out the distillation of aldol with a  $p_H$  lying between 3 and 7. The aldol is first mixed with about three times its weight of water and passed through a continuous column to remove any unchanged acetaldehyde ; it is then heated at  $100^\circ$ – $110^\circ$  in a semi-continuous pot still and column, when crotonaldehyde distils over in the form of an azeotropic mixture, which boils at  $84^\circ$ – $85^\circ$  and separates into two layers on cooling. The upper layer consists of a mixture of about 90 per cent. of crotonaldehyde and 10 per cent. of water, and can be hydrogenated, in either the vapour or the liquid state, by means of nickel according to the methods described in Section II. (pp. 250, 275).

The hydrogenation of crotonaldehyde to butylaldehyde proceeds readily in the liquid phase, but the reduction of the aldehydic radical to the primary alcohol group is more difficult, and best accomplished by vapour hydrogenation.<sup>17</sup>

Many other ethylenic aldehydes and ketones (*e.g.*, ethylideneacetone, phorone, etc.) obtainable by aldol or Claisen condensations, can be hydrogenated, first to the saturated aldehyde or ketone, and then to the corresponding alcohol.<sup>18</sup>

As already stated, butyl alcohol is in increasing demand as a solvent, especially for modern lacquers and spirit varnishes, and the above synthesis from acetylene by a sequence of catalytic actions is applied on a considerable technical scale at the present time.

(b) *Reduction Products of Acetaldehyde*.—It has not yet been proved to be economical, although it is technically feasible, to manufacture ethyl alcohol by the hydrogenation of acetaldehyde. At the same time, since

the process in question has been thoroughly tested on the large scale, it is reasonable to say that, starting from carbide or acetylene, it is practicable to effect the large-scale production of ethyl alcohol and therefore, of course, the wide variety of compounds (ethylene, ether, ethyl esters, etc.) of which alcohol is the starting-point. (Compare Section II., Chapter X, p. 251.)

(c) *Oxidation Products of Acetaldehyde.*—Probably most of the acetaldehyde synthesised technically from acetylene is at once converted into acetic acid by oxidation, and the process about to be described follows immediately after acetaldehyde (resulting from the methods dealt with on pp. 248, 370–376) has been rectified by distillation. Although, therefore, a digression has been made above in order to discuss the condensation and reduction products of the aldehyde, most of the latter is submitted in actual practice to an oxidation process which belongs to the class of catalysis in homogeneous systems which is now under consideration.

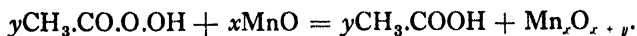
Acetaldehyde is converted into acetic acid by simple passage of a current of oxygen or air, in presence of catalysts which consist of the acetates of certain metals of high and variable valency, notably manganese.<sup>19</sup> The catalyst, however, does not in this case appreciably accelerate the first product formed in the action, for acetaldehyde, if sufficiently pure and dry, absorbs oxygen smoothly and steadily with formation of the highly unstable peracetic acid, or acetyl peroxide :



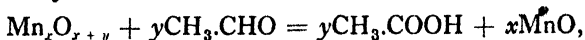
This compound, when obtained in a concentrated condition, is exceedingly explosive and, moreover, sudden decomposition of a relatively small amount will detonate a mixture of acetaldehyde vapour and oxygen; it is therefore essential to keep the concentration of peracetic acid in the charge as low as possible, and certainly of the order of not more than 1 per cent. of the whole, whilst precautions are taken

to prevent condensation of peracetic acid vapour in any isolated parts of the vessel or connections. The main function of the "catalyst" is to effect continuous and smooth decomposition of peracetic acid as formed, a result which is also aided by the use of as high a temperature as is consistent with the vapour tension of acetaldehyde and the pressure which it is safe to employ. In the earlier stages of the process, when acetaldehyde is present in large proportions, this should not exceed 30 lb. per sq. in., but towards the end, so long as practically complete absorption of oxygen (*i.e.*, absence of oxygen in the gaseous phase above the liquid) persists, the pressure is frequently allowed to rise to 60–75 lb. per sq. in.

In presence of manganese acetate the onset of the reaction is marked by development of a deep brown coloration—the manganese present is transformed by the peracetic acid into a higher state of oxidation:—



The higher oxide is reduced immediately by more acetaldehyde:—



and the regenerated manganous salt is ready to reduce more peracetic acid. The catalyst must be present in the form of an organic salt which is comparatively soluble in acetaldehyde.

As already mentioned, pure dry acetaldehyde is capable of immediate absorption of oxygen, but it is necessary to observe these conditions, otherwise little or no action takes place except in the gas phase above the liquid and in these circumstances there is some risk of explosion. Normally, however, the process proceeds rapidly and smoothly in the liquid phase until nearly all aldehyde has been oxidised to acetic acid.

The crude acid is dark brown in colour, owing to the oxidised manganese salt present and to the formation of a minor amount of dark-coloured resinous impurities

(less than 1 per cent. of the product). It is purified by distillation through a fractionating column, one distillation usually yielding an almost colourless acid of 98–99 per cent. purity. The ease with which a "glacial" acetic acid can be produced from the crude product gives the synthetic process a marked advantage over the older process of recovery of acetic acid from wood-distillation acetates of lime.

The working details of the catalytic oxidation of acetaldehyde may be gathered from the following abstract of Matheson's English patent: <sup>20</sup> a closed vessel with suitable resistant lining, *e.g.*, of aluminium, is provided with coils through which water or steam may be passed. An air-pipe is provided, extending to the bottom of the vessel, where it is arranged in spiral form with a multitude of small openings, so that the air is finely distributed over the whole area of the vessel. The vessel is charged with 1,000 gallons of acetaldehyde and about 0.5 per cent. of manganese acetate or other catalyst. Steam or warm water is passed through the coils to raise the temperature to 20°–25°, and air is admitted at a rate of up to 300 cub. ft. per minute. The oxidation takes place with evolution of heat, which is controlled by passing cold water through the coils. The temperature is always maintained not much below the boiling point of the aldehyde under the pressure used and, after the action commences, the pressure is allowed to rise slowly to about 75 lb. per square inch, and the temperature to 65°. Under these conditions the absorption of the oxygen is complete and the nitrogen is allowed to escape through a relief valve after passing through a cold-water condenser at 1°–5°, and a brine condenser at –10° to –15°, each of these being under the same pressure as the reaction vessel. The condensed liquid returns to the reaction vessel through U-seals, and the escaping nitrogen is passed through a scrubber supplied with water at 0°, and maintained at a pressure of 20 lb. per square inch. The reaction is complete in eight to

eighteen hours, after which the contents of the vessel are discharged and the acetic acid is purified by distillation.

In later plants the acetaldehyde is more usually oxidised in solution in acetic acid.<sup>21</sup> This has the advantages of minimising difficulties attendant on the initiation of the reaction, and also of providing more readily for the removal of the heat of reaction and of effecting a higher conversion of acetaldehyde to acid, so that less aldehyde has to be recovered from the exit nitrogen by water scrubbing. The process in this form may be conducted on the batch principle, acetaldehyde being periodically added to a charge already containing acetic acid with some manganese acetate in solution; or acetic acid containing manganese acetate may be allowed to flow down a tower in which it meets a countercurrent of air and acetaldehyde vapour, the process in this case being worked continuously.

A recent patent proposes the conversion of dry acetaldehyde directly into acetic anhydride by oxidation with dry air and/or oxygen at  $40^{\circ}$ – $70^{\circ}$  and 50–100 lb. per square inch pressure in presence of manganese and other metallic acetates.<sup>22</sup>

#### Products Derived from Synthetic Acetic Acid.

Acetic acid is required in large quantities as such, in the form of metallic salts, especially those of sodium, iron, aluminium and lead, and in its many esters which find employment as drugs, perfumes, essences or solvents (the direct technical production of *ethyl acetate* from acetaldehyde has already been noticed (p. 378).

Attention is more particularly directed here to those derivatives of the acid which are largely used in technology, especially in the industries of artificial silk, explosives, lacquers and perfumes.

*Acetic Anhydride*, together with the acid, is needed in immense quantities in the manufacture of acetyl-cellulose, and for other acetylated products of which

the dyestuffs industry and the fine chemical industry (*e.g.*, aspirin and phenacetin) afford many examples. Whilst it is still prepared in quantity by the older methods of the action of sulphuryl (or phosphoryl) chloride on sodium acetate, increasing amounts are produced from ethylidene diacetate (*cf.* p. 373), the latter being synthesised from acetylene and synthetic acetic acid.

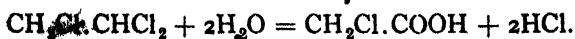
Acetic anhydride is also manufactured by direct thermal dehydration of acetic acid, aided by catalysts; especial activity in developing this method is shown in the patents of British Celanese Ltd.<sup>23</sup> and of the Consortium für Elektrochem. Ind.<sup>24</sup> Acetic acid, when exposed for a brief period to temperatures of 800°–1,000°, is broken down into water, acetic anhydride and keten,  $\text{CH}_2 : \text{CO}$ . In the earlier patents conversion to anhydride by simple passage of the acid vapours through a tube of material which catalysed the dehydration (such as acid-resisting steel, silicon carbide and other substances) at 600°–1,000° was proposed. A later development was the use of phosphoric acid, its salts or esters, as added dehydrating catalysts. Acetic acid may be passed, for example, over sodium metaphosphate or phosphoric acid at 150°–200°, or acetic acid vapours carrying small amounts (0.5 per cent.) of entrained phosphoric acid may be passed through tubes heated at 600°–800°; while, in another form of the process, the acetic acid is momentarily pre-heated to about 800° and passed over a phosphate catalyst at 150°–200°. With suitable precautions (especially as regards the time of exposure to the high temperature) to avoid destruction of the acid by charring, the vapours leaving the process consist of acetic anhydride, acetic acid and water. Since acetic anhydride does not combine with dry steam, it is possible to condense it without re-hydration if the condenser temperatures are maintained above the boiling point of water; but a more efficient method is probably to mix the vapours with

solvent which is immiscible with water, and subsequently to recover the acetic anhydride by fractional distillation from the organic solvent. It is also possible to employ certain low-boiling organic solvents in the form of vapour in the fractional condensation of acetic anhydride above  $100^{\circ}$ ; the vapours from the converter are mixed with those of such liquids as benzene, carbon tetrachloride or light petroleum, and the latter assist in entraining the water and acetic acid vapours from the acetic anhydride as it condenses. The thermal treatment of acetic acid is becoming increasingly important as a means for manufacture of acetic anhydride.

The residual dilute acetic acid from these operations is, of course, re-concentrated and re-processed. At this point it may be useful to direct attention to some modern, although not catalytic, processes for concentration of dilute acetic acid solutions. Certain of these <sup>25</sup> depend on extraction of the acid by a suitable liquid solvent, followed by recovery of the concentrated (90–97 per cent.) acid from the solution by distillation, according to methods first introduced by H. Suida. In one form of the process, the dilute acetic acid is treated with cresols (or wood-tar oils) so as to obtain most of the acid in solution in the cresol; the cresol solution is then distilled with a petroleum fraction (b.p.  $100^{\circ}$ – $120^{\circ}$ ) which facilitates the removal of the acetic acid as an azeotropic mixture (b.p.  $110^{\circ}$ ) with the petrol, and this latter mixture is resolved, on treatment with a trace of water, into its components. Other modifications of the procedure are also in use; in the preliminary separation other liquids may be employed, such as butyl or amyl acetate, ethyl phthalate, decalin, etc. In modern acetic acid recovery plants using the Suida process the efficiency of recovery reaches 95–96 per cent.; descriptions of the layout and operation of such plants have been given by N. W. Krase,<sup>26</sup> H. Guislot<sup>27</sup> and E. P. Partridge.<sup>28</sup> *Chloracetic Acid* (see also p. 438), obtained by



chlorination of acetic acid, is an important intermediate in the production of synthetic indigo ; an alternative proposal for its manufacture consists in the action of sulphuric acid at 160°–190° on trichlorethylene :—



*Acetone* is needed in large quantities as solvent and for other purposes. As already stated, fermentation, wood-distillation, or direct catalytic production of acetone from alcohol or acetylene are the methods now in use, but it has been manufactured from acetic acid both in Europe and America by catalytic decomposition of the acid vapours in presence of alumina or lime, as described in Section II., Chapter X (p. 259). The process as used at Shawinigan consisted in passing the pre-heated vapours of synthetic glacial acetic acid through steel tubes, 13 ft. long and 1 ft. in diameter, containing rough cast-iron balls coated with hydrated lime mixed with a small quantity of magnesia. At 483°, 95 per cent. of the acid was converted into acetone; the vapours from the tubes were scrubbed in a soda-tower, and the aqueous acetone was then rectified in a continuous still.

#### \* The Production of Ethyl Alcohol from Ethylene.<sup>29</sup>

The olefine gases, of which ethylene is the most common and important, are not met with in technology to the same extent as acetylene, but they are present in fairly large amounts in several industrial gases, and it is probable that the latter will find increasing use as sources of ethylene and, perhaps to a less extent, of higher olefines. Ethylene, for example, can be transformed into a number of useful aliphatic products ; it can be made readily to combine with chlorine, when useful solvents result, or with hypochlorous acid, forming ethylene chlorhydrin. Both of these products can be further acted upon, with the result

\* For references to the production of power alcohol by fermentation processes, see Section III, Chapter I, p. 327.

that a way is opened for the manufacture of ethylene glycol and its derivatives (*e.g.*, the dinitrate) from ethylene. Processes of these types (which, not involving catalytic action, are strictly outside the province of this volume) are already in operation in America and elsewhere; a process of a semi-catalytic nature which deserves mention here, however, is the conversion of olefines into alcohols by absorption in concentrated sulphuric acid.

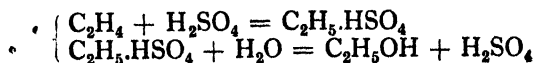
Before describing this, it may be stated that the chief sources of cheap ethylene (accompanied by smaller proportions of propylene, butylenes, amylenes and diolefines) are as follows:—

(a) The "natural gas" which escapes in large quantities from many of the oil-bearing strata of America and elsewhere;

(b) "Cracked gas," that is, the mixture of gaseous hydrocarbons and hydrogen produced when heavy petroleum oil is submitted to pyrogenetic decomposition in the manufacture of cracked petroleum spirit—a very large industry;

(c) Coke-oven gas—the gaseous compounds produced in the distillation of coal for various purposes, for example, producer-gas, illuminating gas, or for metallurgical coke.

The production of alcohol from ethylene by absorption in sulphuric acid



has been studied exhaustively on the large scale, but it does not appear that alcqhol is made industrially at present in any great amount by this process. An account of work carried out at the Skinningrove Iron and Steel Company's works, North Yorkshire, indicates that coke-oven gases containing about 1.7–1.8 per cent. of ethylene (after scrubbing in 80 per cent. sulphuric acid to remove moisture and higher olefines) can be absorbed efficiently in sulphuric acid of 95 per

cent. strength at  $80^{\circ}$ – $85^{\circ}$ . Above this temperature carbonisation of the organic compounds and formation of sulphur dioxide sets in. In a tower scrubber 18 per cent. of the sulphuric acid present can be combined with ethylene, but if further scrubbing of the gas in a mechanically agitated washer supervenes, the conversion is considerably higher. The absorption is accelerated in presence of silica.

Acid of higher concentration than 95 per cent. causes diethyl sulphate and even carbyl sulphate to be produced.

In order to obtain the free alcohol, the spent acid is diluted with water to 64 per cent. concentration and then distilled under reduced pressure (at  $94^{\circ}$ – $146^{\circ}$ ). The residual acid (which is free from alcohol) is then of 80 per cent. strength.

The experiments indicate that an alcohol plant to deal with the coke-oven gases from a carbonisation of 800 tons per day would require the use of nine towers 10 ft. in diameter and 80 ft. high; if 70 per cent. of the ethylene were absorbed and, of this, 70 per cent. were recovered as alcohol, the daily production of the latter would be about four tons.

Put in another way, it is estimated that 1.6 gallons of absolute alcohol could be obtained from each ton of coal carbonised, equivalent to a total possible annual production of 59,000,000 gallons of alcohol from the 37,000,000 tons of coal carbonised in gasworks and coke-ovens in this country; obviously, owing to the elaborate installation necessary and for other reasons, the practical output could only be a fraction of the total amount potentially available.

Damiens<sup>30</sup> has observed that sulphates of various metals, notably cuprous sulphate, stimulate the absorption process.

In order to produce diethylsulphate (required to some extent in the dye and fine chemical industries for ethylation), Curme<sup>31</sup> has proposed to conduct the absorption in more concentrated sulphuric acid.

More recent proposals for the hydration of ethylene avoid the use of sulphuric acid and consist in the direct union of ethylene and steam at high temperatures and pressures in presence of an appropriate solid catalyst. Thus, it is stated<sup>32</sup> that alcohol is produced when ethylene, mixed with an excess of steam, is passed over thoria or phosphoric acid mounted on charcoal at  $400^{\circ}$ – $500^{\circ}$  and 25–200 atmospheres pressure at a space velocity of 10,000–50,000 litres of gas (at N.T.P.) per hour per litre of catalyst; with cadmium or other phosphates at  $100^{\circ}$ – $300^{\circ}$  and 70 atmospheres pressure,<sup>33</sup> or by passage of ethylene and steam over sodium hydrogen sulphate<sup>34</sup> at  $150^{\circ}$ – $160^{\circ}$  or a boric-phosphoric acid catalyst at  $200^{\circ}$ – $270^{\circ}$  and up to 20 atmospheres pressure, the same result is obtained. In all cases, however, the conversion of ethylene to alcohol at each passage over the catalyst is very small, not exceeding 1 per cent.

Comprehensive studies of the equilibrium of the vapour-phase hydration of ethylene in presence of phosphate or alumina catalysts at  $400^{\circ}$  and varying pressures have been made.<sup>35</sup> The calculated equilibrium conversion is 8 per cent. at 200 atm. and 27.5 per cent. at 1,000 atm., but in practice these figures have not been approached.

Finally, a group of American chemists<sup>36</sup> connected with the Standard Oil Company has carried out considerable work on the fixation of olefines by sulphuric acid, and has found that the presence of mineral oil with the sulphuric acid leads to more efficient fixation of the ethylene; they also report the successful production and isolation on a commercial scale of the secondary propyl, butyl, amyl and hexyl alcohols (of the general formula  $\text{CH}_3\cdot\text{CH}(\text{OH})\cdot[\text{CH}_2]_n\cdot\text{CH}_3$ ) from propylene, butylene, amylene and hexylene present in "cracked gas."

It has been mentioned earlier in this chapter that isopropyl alcohol is used in perfumery and for other purposes; secondary butyl alcohol can be converted into methylethylketone by dehydrogenation (*cf.* p. 249),

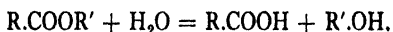
whilst this alcohol and the corresponding amyl and hexyl compounds are useful as solvents and to a smaller extent for synthetic purposes.

## CHAPTER II

### ACTIONS OF HYDROLYSIS IN LIQUID SYSTEMS

THE production of esters from an acid and excess of alcohol is greatly accelerated (and the conversion increased) in presence of small concentrations of strong acids, and similarly the latter catalyse the resolution of an ester in presence of excess of water into its component acid and alcohol.

This is usually attributed to the catalytic (hydrolytic) action of the hydrogen ion, so far as hydrolysis in an aqueous solution is concerned :—



In general technical practice, the use of acid hydrolysis of a simple ester is rarely employed, for in the majority of cases the manufacturer is concerned to synthesise, not to break up, an ester ; and, as this reaction has already received theoretical treatment in Section I. (pp. 57, 60), no purpose will be served here by enlarging further on the practical details involved.

The principle in question is applied technically, however, in the acid hydrolysis of natural complex carbohydrates, when simple hexose sugars are produced ; and some account of the technical conversion of starch and cellulose material into sugars by means of acids is therefore necessary.

Such transformations are also carried out to a great extent in industry in the course of processes of fermentation, for example, the production of alcohol from malt or from molasses ; these hydrolytic actions, and also the lipase hydrolysis of fats, have already been considered in Section III. from the general standpoint of catalysis by enzyme action.

There remain two or three other important instances of technical hydrolytic actions accelerated by non-enzymic or ordinary catalytic agents, which will be quoted as further examples of the industrial applications of catalysis in this field. Firstly, there are three independent methods (each of which is employed widely) for the hydrolysis of that important class of esters, the fats ; and, in the next place, the commercial production of benzaldehyde and benzoic acid from chlorinated toluene (benzalchloride and benzotrichloride) deserves consideration as an example of this type of process.

#### Conversion of Starch into Simple Carbohydrates by Mineral Acids.<sup>1</sup>

This process has a two-fold importance ; it has been employed for a long time in the manufacture of glucose for sweetening and edible purposes, and it has also been used, and will probably be used on a larger scale still, for the conversion of starches into readily-fermentable products. Chemically the two aspects of the industry are the same, but in the latter case the final objective is not a crystalline sugar or sugar syrup, but a solution which can be fermented to yield alcohol for potable, industrial, or fuel and power purposes.\*

*Manufacture of Crystalline Glucose or of Sugar Syrup.*—The raw materials subjected to the process vary according to the country ; thus in England, rice, sago, maize and potatoes are used, in Germany mainly potatoes, and in North America maize is by far the most common starting-point. The acids employed also vary according to local conditions and, whilst hydrochloric acid is most generally used in the United States, sulphuric acid is the usual medium in England.

The process is purely catalytic and dependent on the hydrogen ion concentration of the system ; the actual proportion of aqueous acid to starch has little influence

\* See also Section III, Chapter I, p. 327.

on its course. The ultimate desired action is summarised in the equation



but this by no means depicts what actually takes place. The first products of degradation of the starch are dextrins and maltose, whilst glucose is probably also present from the commencement of hydrolysis.

Dextrins are carbohydrates intermediate in complexity between disaccharides, such as maltose, and starch or cellulose, and probably comprise about four hexose units condensed together in the dextrin unit. Like disaccharides, they are freely soluble in water, but, unlike these, are insoluble in 70 per cent. alcohol; whilst disaccharides do not react with iodine, dextrins give a reddish-brown colour in place of the familiar deep blue-black colour given by starches.

Maltose is a disaccharide made up of two condensed molecules of glucose, and further action of the acid, either on dextrin or maltose, produces glucose; glucose itself is slowly attacked by the mineral acid if the concentration of the latter or the time of contact be too great.

The conversion, as a matter of fact, proceeds very rapidly. Formerly, it was carried out in open, lead-lined wooden converters with a 5 per cent. solution of sulphuric acid in water, two parts of starch being mixed with five parts of the aqueous acid solution; complete conversion to glucose by this means requires treatment for four or five hours. In modern factories the operation is usually effected in closed converters of copper or gun-metal under a steam-pressure of 10-30 lb. per sq. in., *i.e.*, at about 110°-125°. The acid concentration necessary is then only 0.5-0.6 per cent., and complete hydrolysis to glucose takes place in about one and a half hours. In the latter case the liquor is tested with iodine until the absence of the reddish-brown tint shows that dextrin has disappeared, but in order to produce sugar syrup (syrup of glucose, corn syrup) partial hydrolysis only is effected,



and the carbohydrates present in the finished syrup consist of about equal proportions of dextrin and glucose with about 20 per cent. of water, the hydrolytic action only occupying thirty to fifty minutes as a rule.

The acid liquor is nearly neutralised with carbonate of lime (sulphuric acid) or soda-ash (hydrochloric acid), settled and filtered; the filtrates are evaporated to a certain extent, passed through decolorising charcoal (char) and further concentrated in a vacuum evaporator to syrup of the desired moisture content, or to crystallisation, as the case may be. In the latter case crystalline glucose is separated by cooling and centrifuging.

*Conversion of Starch Materials into Fermentable Sugars.*—The technique of this process is the same as that given above, but the raw material employed depends on local and other conditions. For potable alcohol, and also for industrial alcohol, rice-starch and potato-starch are used in Europe and also, together with maize, in America. It is stated by the Department of Scientific and Industrial Research that more suitable home sources of fermentable sugars for industrial and power alcohol would probably be man-golds and Jerusalem artichokes. In the Dominions and India other suitable sources of starch include cassava, sweet potatoes, arrowroot, etc., as well as rice and maize.

#### Conversion of Cellulose into Fermentable Sugars by Mineral Acids.

The degradation of the cellulose system into its component monosaccharides is unfortunately much more difficult to achieve completely than that of starch. Vast quantities of cellulose occur in nature in the form of practically useless material, for example, the abundant grasses of the tropics, Australia and South America, the straw of maize, rice and other cereals, the chaff or husks of many seeds, cotton-seed hulls,

maize cobs, etc., etc., and sawdust and waste small wood from cut timber.

The dilute acid process referred to above has a certain effect on cellulose material, and is employed to an increasing extent in North America and elsewhere ; but whilst, expressed in terms of final yield of alcohol, one ton of starch gives a practical output of 80 gallons of 95 per cent. alcohol, one ton of cellulose yields only 20-25 gallons of the spirit in practice. The reason for this is that cellulose material is composed of three types of complex carbohydrate material, cellulose, lignocellulose and hemicellulose, and only the latter is readily hydrolysed by dilute aqueous acid. The proportion of hemicellulose present is usually about 25-40 per cent., and it is this part of the whole fibre which is convertible into monosaccharides. Of the latter, a considerable proportion, depending on the species of the original plant, may be pentoses (xylose) and not the yeast-fermentable hexose glucose, but in such cases processes are available (*cf.* Section III., pp. 355-358) for fermentation by means of appropriate bacterial cultures, which produce ethyl alcohol with, in some cases, acetone as a secondary product.

The manipulation of the dilute acid hydrolysis is much the same as in the case of starch, but the action proceeds at a slower rate. Working under pressure and at a concentration of about 0.6 per cent. sulphuric acid, about four or five hours is required ; whilst with 2 per cent. acid at atmospheric pressure the operation takes at least seven hours.

A useful modification of the method, economising space and volume of aqueous acid used, consists in soaking the dried wood waste with acid of 1-2 per cent. strength, when the cellulose material will take up at least its own weight of liquid and still remain dry enough to handle. It is then either steamed at atmospheric pressure or passed through a steam-jacketed worm conveyor, where it is heated externally by steam at 80-100 lb. per sq. in. pressure.

In either case the finished product still contains at least 70 per cent. of insoluble cellulose, and the soluble portion is extracted in diffusion batteries similar to those used in the beet-sugar industry. The further treatment of the aqueous extract prior to fermentation is the same as in the case of the starch processes.

Much research has been undertaken in order to convert the more refractory constituents of cellulose into soluble sugars, and it appears probable that the employment of concentrated or gaseous hydrochloric acid in place of dilute aqueous acid effects the desired hydrolysis and permits of the production of 80 gallons of industrial alcohol per ton of cellulose material.<sup>2</sup> The practical difficulties involved in the large-scale application of this process are evidently formidable, but there is little doubt that they will be surmounted in due course.

The primary incentive to applied research in this field is, of course, the desirability of producing power alcohol on a large and economic scale, but it should be borne in mind that, apart from this main object, the production of sugars of various types *per se* is of possible commercial interest, although at present of subsidiary importance.

Whilst dealing with the subject of cellulose degradation, passing reference may be made to the presence of sugars in the waste liquor from the sulphite process for the conversion of cellulose into paper; these liquors, which, after suitable treatment, are fermentable, correspond in character with the aqueous extracts produced by the above acid processes.

#### Hydrolysis of Fats.

When fats are to be converted into soaps, it is usually most economical to hydrolyse them directly with aqueous soda (or potash), thus at once producing the soda (or potash) soaps, which are ready, after washing and cleansing, for mechanical transformation.

into bars, tablets, powders, or other form in which they pass into the market.

When the fatty acids are required as such for other purposes, for example, candle manufacture or leather-dressing, the saponification process, followed by liberation of the free acids by mineral acid, is somewhat cumbersome. Moreover, it is evident that the expense of caustic soda could be avoided if water alone were employed as hydrolytic agent; and, even for soap-making, caustic soda could thus be replaced by the cheaper soda-ash, which would be used subsequently to neutralise the liberated fatty acids. Also, since concentration and recovery of the glycerine simultaneously set free from the fats is an important economic feature of fat-hydrolysis, processes which lead to the formation of a comparatively concentrated glycerine liquor (e.g., 15–16 per cent. glycerine) have an important advantage in this respect over the ordinary saponification, in which the lyes usually contain only 3–5 per cent. of glycerine.

Fats can be hydrolysed by water alone, but the temperature necessary ( $200^{\circ}$ – $220^{\circ}$ ) before the action proceeds at a technically useful speed is too high for economical working, involves an equivalent steam pressure of nearly 250 lb. per square inch, and leads to serious discoloration of the fatty acids produced. Certain basic oxides, however, exert a powerful catalytic effect on the rate of hydrolysis, and complex fatty-aromatic sulphonic acid derivatives known as the *Twitchell hydrolytic agent* are equally serviceable as catalysts in the splitting of fats, whilst sulphuric acid alone is a useful fat-splitting agent in the case of very crude materials. All these methods, and also the lipase fermentation process which has already been referred to in Section III. (p. 361), are employed on the large scale in the production of fatty acids, and are instances of technical hydrolysis promoted by catalytic means.

*The Autoclave Process of Fat-hydrolysis.*—Hydrolysis

in presence of basic oxides (especially lime, magnesium and zinc oxide) is termed in works practice the "autoclave process," owing to the action being carried out in pressure-agitators at about  $140^{\circ}$ – $150^{\circ}$  (100–120 lb. per square inch steam pressure). This process is in fairly wide use, more especially when the fatty acids themselves are the objective, and it can be completed in the same time as that necessary at 250 lb. per square inch pressure of steam in the absence of the catalytic bases. It is carried out in stout vertical cylindrical vessels with dished ends, steam-jacketed or fitted with an internal closed coil; sometimes mechanical stirring is used; more frequently agitation is effected by a current of steam, distributed into the lower part of the vessel by a perforated pipe and maintained by the continuous withdrawal of a certain amount of steam from the head of the vessel.

The autoclave is charged to about 70–80 per cent. of its capacity with a mixture of about 80 parts of fat and 20 parts of water, together with about 3 parts of lime, or a mixture of lime and zinc dust. (The zinc dust, which contains both metallic zinc and oxide, serves as a catalyst and also aids in preserving the acids from undue discoloration; the latter function is probably due to the reducing action of the metallic zinc present.) The concentration of basic oxide which experience has shown to be desirable is abnormally high for a strictly catalytic operation, and is about 30 per cent. of that necessary to neutralise the total fatty acid produced.

The autoclave is kept at a pressure of 100–120 lb. per square inch for ten or twelve hours, during which hydrolysis proceeds, according to the law of mass action, at a rate which is governed by the amount of unsaponified fat present. Thus 90 per cent. of the fat is usually hydrolysed in from three to five hours, but conversion of 98–99 per cent. of the fat to fatty acids requires, as stated, ten to twelve hours. When the latter stage has been reached the contents

of the autoclave are blown into a wood-lined tank (well lagged externally), in which they can settle slowly while still warm. After some hours the lower layer of aqueous liquor ("sweet water"), which may contain up to about 15 per cent. of glycerine, is drawn off for evaporation to crude glycerine; the upper layer of fatty acid and lime soap is boiled up by means of steam, sufficient dilute sulphuric acid is added to neutralise the lime present, and the fatty acids are settled and finally washed by further boiling with water.

*The Twitchell Process of Fat-hydrolysis.*—In 1900, Twitchell<sup>3</sup> published details of a catalyst or "emulsifying agent" by means of which fats could be completely hydrolysed by water below 100°. The agent in question was prepared by treating a mixture of oleic acid and benzene or, better, naphthalene, with concentrated sulphuric acid; sulphonation and condensation took place, the resulting product (when naphthalene was employed) being apparently of the general formula,  $\text{COOH.C}_{17}\text{H}_{34}(\text{C}_{10}\text{H}_8).\text{SO}_3\text{H}$ .

The agent, after being washed free from sulphuric acid, is employed in about  $\frac{1}{2}$ –1 per cent. concentration on the fat to be hydrolysed.

The process is carried out in a wooden vat with a loose lid, fitted with a perforated copper coil for the admission of steam. The fat, which should have been clarified previously by boiling with dilute sulphuric acid and settling, is run in, together with about 50–100 per cent. of its weight of water, and the Twitchell agent in the proportions stated. The mixture is maintained in a state of gentle ebullition throughout the process by a current of steam from the open coil. After a period of induction, hydrolysis sets in fairly rapidly, the rate declining steadily as the concentration of neutral fat diminishes; the process usually takes from one to three days for completion. Time is saved by interrupting the charge when it is about half-hydrolysed, settling and drawing off as much aqueous glycerine as possible, adding more water

to replace that withdrawn and resuming the operation.

A conversion of 97-98 per cent. of the fat to fatty acids is usually reached before the latter are worked up (by boiling with a little free sulphuric acid until all emulsion is destroyed; the acids are then settled and washed with boiling water).

The Twitchell process is used largely in America and, to some extent, on the Continent, but does not appear to make very great headway in England. Its advantages are cheapness of reagents and low steam consumption combined with a concentration of glycerine in the aqueous liquors which approaches that of the autoclave process. *Per contra*, the hydrolysis is somewhat slow by comparison with the latter, and there is a tendency to the production of dark-coloured fatty acids.

M'Kee and Lewis<sup>4</sup> substitute *p*-cymene for naphthalene in the agent, and hold that this leads to less discoloration and more rapid action; whilst the Vereinigte Chemische Werke<sup>5</sup> reach the same end by employing a similar product obtained by sulphonation of a mixture of naphthalene and hydrogenated castor oil acids.

Theoretically, these agents are interesting in their close simulation of what may be supposed to be the essential structure of a typical hydrolytic enzyme (*cf.* Section III, Chapter V, p. 362).

*Acid-hydrolysis of Fats.*—If a completely dry neutral fat is intimately mixed with about 5-8 per cent. of 96 per cent. sulphuric acid and heated at 110°-120°, with mechanical agitation and admission of dry steam, for about eight to twelve hours, complete hydrolysis is effected. This result depends on the catalytic action of the mineral acid, which is mainly hydrolytic, but also partially that of a sulphonating agent (aliphatic sulphonic derivatives being produced and broken down by the elements of water into hydroxy-fatty acids and regenerated sulphuric acid).

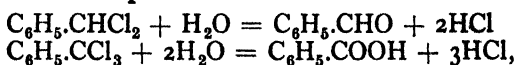
As might be anticipated, the resulting fatty acids

are extremely dark in colour, whilst much of the liberated glycerine is destroyed by the action of the sulphuric acid. It is therefore necessary to submit the crude fatty acids to purification by distillation in a current of super-heated steam, and in practice, although used on quite a large scale, the process is applied in general only to low-grade fats, such as bone greases, etc., the glycerine in which is hardly worth recovery and the fatty acids from which, in any case, would require distillation in order to render their colour satisfactory.

#### Production of Benzaldehyde and Benzoic Acid from Chlorinated Toluene.

The process chiefly employed for the manufacture of benzaldehyde consists in chlorinating toluene, when a mixture of benzalchloride,  $C_6H_5.CHCl_2$ , with benzotrichloride,  $C_6H_5.CCl_3$ , is formed. If it is desired to obtain benzoic acid as main product, the chlorination is carried on until the toluene is transformed almost entirely into the trichloride.

Either chloride, when heated with aqueous caustic soda or milk of lime, passes into the corresponding hydroxylated compound :—



but the conversion is slow unless the action is carried out above  $100^\circ$  (i.e., under a moderately high pressure).

Schulze<sup>6</sup> found that the presence of metallic iron or iron salts accelerated the hydrolytic action of water—so much so that under these conditions rapid decomposition occurred at or below  $100^\circ$ ; the catalysed action is conducted as follows :—

• (a) *Benzalchloride containing Benzotrichloride as By-product.*—Sixty parts of benzalchloride are gently warmed with 10–15 parts of water, and 0.02 parts of metallic iron in powder form (or of an organic salt of iron) are added, after which the mixture is heated to about  $95^\circ$ . Hydrolysis then sets in, and



hydrochloric acid distils off and is absorbed in the usual way in a water-scrubber or tower; when the process slows down, 9 parts of quicklime, slaked to a thin paste with water, are added and the liquor is steam-distilled. Benzaldehyde passes over, and the residual liquor is worked up for calcium benzoate or benzoic acid.

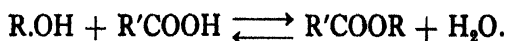
(b) *Benzotrichloride*.—When benzoic acid is the main product, it is usual to add the alkali at the commencement of the operation, milk of lime from 34 parts of quicklime being used, whilst the proportions of the other reactants remain as in the first example.

This process is generally the cheapest source of benzaldehyde and benzoic acid, but the products, especially benzaldehyde, retain traces of chlorine compounds which make them unsuitable for use in edible products or high-grade perfumes. For most other purposes (*e.g.*, use in industrial synthetic operations) benzaldehyde and benzoic acid from chlorinated toluene are sufficiently pure.       •       •

## CHAPTER III

### ESTERIFICATION AND DEHYDRATION OF ALCOHOLS BY MINERAL ACIDS

THIS group of processes--the elimination of the elements of water from an alcohol and an acid yielding an ester, or from an alcohol alone to give an ether or a hydrocarbon--is equal in technical importance to the hydrolytic actions which were reviewed in the preceding chapter. The theoretical principles of esterification were referred to in Section I. (pp. 58, 60), and it must suffice here to indicate the relationship of technical practice to theory. Thus it may be pointed out, in the first place, that in some cases it is possible to obtain efficient conversion of an alcohol to an ester solely by conforming to the law of mass action which, as Berthelot and St. Gilles<sup>1</sup> showed in 1862, controls the changes represented in the system



If it is possible to remove one of the components of this system continuously (*e.g.*, to withdraw water by evaporation) the process will tend to become complete in one or other direction. Thus, for example, glycol or glycerol, when heated with equivalent weights of higher fatty acids under reduced pressure, passes smoothly into the neutral fatty esters or synthetic fats (Schlinck,<sup>2</sup> Franck<sup>3</sup>); in such cases adequate conversion to ester is secured by employing conditions of temperature and pressure which ensure removal of water as fast as it is formed, without the intervention of a catalyst.

In many instances, however, one or more of the components of the system--alcohol, acid or ester--is appreciably volatile, and here recourse is frequently

had to the aid of catalysts, which may be either solids at the surface of which the gaseous alcohol and acid interact, or, as happens most frequently in technical practice, the catalytic esterification may proceed entirely in the liquid phase (*cf.* Section I., Chapter IV, pp. 57-67).

The catalysts employed in technical esterifications in the liquid phase are almost exclusively strong mineral acids, especially hydrochloric acid, sulphuric acid and phosphoric acid. Sulphuric acid probably antedates the others in its use in this connection, which extends back to the researches of Williamson<sup>4</sup> and even earlier; its efficiency was formerly considered to be due to its affinity for water, but this view has been shown by Senderens and Aboulenc<sup>5</sup> (1911 and later), and by Bodroux<sup>6</sup> to be inadequate. These workers found that the presence of very small proportions (*e.g.*, 1 per cent.) of sulphuric acid was capable of effecting very high conversions to ester in many cases, and that similar concentrations of anhydrous aluminium sulphate produced the same order of results, whereas an anhydrous neutral salt (*e.g.*, sodium sulphate) was ineffective. The action must, therefore, be ascribed to catalysis as opposed to the mere fixation of water by the agent employed. Many years ago, also, it was observed by Victor Meyer and Sudborough<sup>7</sup> that, in the preparation of organic esters, sulphuric acid could be replaced by a saturated solution of hydrogen chloride in the alcohol employed, esterification thus proceeding in due course at room temperatures; at about the same time, Emil Fischer and Speier<sup>8</sup> introduced the use of an alcoholic solution containing about 0.5-1 per cent. of hydrogen chloride, rapid and relatively complete esterification being effected in many cases when organic acids were boiled under a reflux condenser with this agent for a relatively short time.

The choice of mineral acid in technical practice is determined by several considerations. Sulphuric acid

is somewhat cheaper, it is non-volatile, and therefore does not yield acid vapours (so that only the still portion of the plant comes in contact with mineral acid), and it is easily removed by washing the finished product with water; on the other hand, its charring and generally violent action may be inconvenient in the case of many organic compounds. Hydrochloric acid is perhaps not quite so efficient on the whole as sulphuric acid, and it passes to some extent into the vapour phase; yet it is milder in its general action on the more delicate organic derivatives and in many instances gives rise to a smaller or insignificant amount of undesired by-products.

The use of these agents will be illustrated by a brief description of the industrial preparation of some typical esters, acetals, ethers and olefines.

*Esters.*—Many esters have technical importance as solvents, perfumes (including “fixatives”), medicines and, lately, as textiles (cellulose acetates). We are concerned here solely with the extent to which their manufacture involves homogeneous catalysis, and the discussion will be oriented primarily with respect to the methods adopted. The acetates form a large and important section of the industrially useful esters, and afford a suitable background upon which to illustrate the application of several catalytic processes.

*Ethyl Acetate.*—This is one of the most important esters used in industry, both as a solvent and in other ways. Several alternative processes exist for its manufacture, and it should first be recalled that modern practice utilises acetaldehyde as the raw material (*cf.* p. 378), the aldehyde being “polymerised” to ethyl acetate by aluminium ethylate, a reaction first noticed by Petrenko-Kritschenko<sup>9</sup>; as already indicated in Chapter I. of this Section, this method is quite possibly destined to supersede the other esterification processes based on alcohol and acetic acid.

(Here it may be mentioned that an analogous catalytic transformation<sup>10</sup> of an aldehyde to a corre-

sponding ester is used in practice for the manufacture of the perfume (artificial musk solvent) *benzyl benzoate* : 100 parts of benzaldehyde are heated to about  $110^{\circ}$  and stirred thoroughly whilst a hot solution of 1 part of sodium in 20 parts of benzyl alcohol is added. A vigorous action occurs, which may be summed up as



The product is recovered by steam-distillation, after acidification of the diluted mass with dilute acid, followed by fractional distillation to eliminate the free benzyl alcohol present.)

Older methods of production of ethyl acetate include the heating and subsequent distillation of acetic acid with some excess of ethyl alcohol in presence of hydrochloric acid, anhydrous calcium chloride or, more frequently, sulphuric acid in amount equal to not more than 5 per cent. of the interactants. Aromatic sulphonic acids, especially naphthalene- $\beta$ -sulphonic acid, have also been employed as catalysts of esterification, but probably sulphuric acid is used to a much greater extent than any of the other substances. When operating on the intermittent system a first distillate of ethyl acetate, alcohol, water and some acetic acid is obtained, the sulphuric acid being usually run to waste ; the crude ester is washed with carbonate solution and distilled over calcium chloride in order to free it from both alcohol and water. Comparatively recently, Backhaus,<sup>11</sup> Durrans<sup>12</sup> and others, have patented plant for the continuous production of ethyl acetate by the sulphuric acid method, the general scheme being to cause a pre-heated mixture of alcohol and acetic acid with about 3 per cent. of sulphuric acid to enter and flow down the lower part of a fractionating column. The esterified mixture passes up the column through plates of the usual type, and ethyl acetate containing some alcohol is recovered from the top and subjected to further purification as required.

The sulphuric acid method (employing 3-5 per cent.

of the acid in the reaction mixture) is similarly used in the preparation of the following esters from their constituent alcohols and acids :—

- *Amyl acetate* (solvent),
- Methyl and amyl salicylates* (perfumes and medicines),
- Benzyl and bornyl acetates* (perfumes),
- Methyl and ethyl benzoates* (perfumes),
- Ethyl succinate* (fixative for perfumes).

The details of procedure vary with the compounds in question: thus, if the alcohol is more expensive than the acid and is of similar boiling point to the ester (as often happens), an excess of acid instead of alcohol is employed. The temperature of treatment also varies: thus, whilst the more volatile compounds are refluxed and finally distilled direct from the reaction mixture, in other cases (*e.g.*, methyl salicylate), the process is undertaken at about  $100^{\circ}$ – $120^{\circ}$ , followed either by removal of the (relatively high-boiling) product under diminished pressure or by preliminary removal of the mineral acid by washing with water, distillation being subsequently carried out. In a few instances (*e.g.*, bornyl acetate) the esterification is carried on at quite a low temperature in order to avoid undesired side reactions.

It has already been mentioned that sometimes the use of sulphuric acid is quite inadmissible owing to its destructive action on the organic compounds present, and that in such cases, following the Fischer-Speier method, anhydrous hydrogen chloride is used in technical practice. This is well illustrated by the perfume fixatives *ethyl succinate*, *ethyl citrate* and *ethyl lactate*: the first of these may be prepared by refluxing 10 parts of succinic acid with 15 parts of alcohol in presence of 0.5 parts of sulphuric acid, distilling off the excess of alcohol, cooling, diluting with water, neutralising, and fractionating the neutral ester; but the last two are best manufactured by passing

dry hydrogen chloride into solutions of the acids in a similar excess of alcohol, standing or heating at about 50° for twelve to twenty-four hours and distilling under reduced pressure after removal of the free hydrochloric acid.

Other examples in which the hydrochloric acid method is preferable are those of *methyl* and *ethyl cinnamates* and of *methyl anthranilate*, each of which is important in perfumery.

*Acetylations with Acetic Anhydride or Acetyl Chloride.*—In yet other instances, the use of any mineral acid is inapplicable owing to the ready isomerisation of the alcohol present under these conditions; this obtains especially in the case of terpene alcohols, such as geraniol, linalool and menthol, the acetates of which are in demand in perfumery. Further, the hydroxyl groups of phenols, of cellulose, and some other compounds are not readily esterified by organic acids in presence of mineral acid catalysts. In both these cases recourse is usually had to acetic anhydride (or, less frequently, acetyl chloride) in order to introduce the acidic radical.

It is well known that the acetylating action of acetic anhydride proceeds more rapidly, and at a lower temperature, in presence of a small proportion of anhydrous sodium acetate, or of anhydrous zinc chloride. The mechanism of the intervention of these materials, although not precisely understood, is undoubtedly catalytic in nature, and these processes fall within the group of esterification methods now under review. They are used technically, for example, in the production of *acetates of linalool, menthol and geraniol and of acetylsalicylic acid* (aspirin, cf. below). Thus a mixture of 5 parts of linalool or geraniol, 3 parts of acetic anhydride and 1 part of anhydrous sodium acetate may be well stirred at 100°–110° for some hours, and then worked up by decomposition of unchanged anhydride with water followed by fractionation under reduced pressure in the usual manner.

Less frequently acetyl chloride is used as acetylating agent in the cold in presence of pyridine. This procedure, more familiar in the laboratory in the case of benzylation, is, however, not catalytic, since the function of the tertiary base present is to fix the hydrogen chloride liberated in chemical combination, and an excess of the base is usually employed.

Finally, it should be mentioned that in one or two notable industrial processes of acetylation, the action is catalysed by sulphuric acid, although, in order to effect complete acetylation, it is necessary to employ a certain amount of acetic anhydride in admixture with acetic acid. This statement applies to the preparation of acetylsalicylic acid and of cellulose acetates.

*Acetylsalicylic Acid (Aspirin).*—In addition to non-catalytic methods of manufacture, the use of acetic anhydride assisted by sulphuric acid is widely practised. One hundred and thirty-eight kilograms of salicylic acid are dissolved in 120 kg. of acetic anhydride containing 0.5 kg. of concentrated sulphuric acid and heated at  $50^{\circ}$ – $60^{\circ}$  for some time, finally increasing the temperature to  $90^{\circ}$ . The product is cooled to  $0^{\circ}$  with agitation, and separated acetylsalicylic acid is filtered off and washed with water at  $0^{\circ}$ , and later with toluol. The filtrates and washings are worked up for acetic acid, unchanged acetic anhydride and unchanged salicylic acid, whilst the acetylsalicylic acid is purified by recrystallisation.

*Cellulose Acetates.*—The acetylation of cellulose has, of course, developed of late years into a very large industry, and a full description of the technique of the various patented processes at present used is beyond the scope of the present work. The rate of acetylation and the character of the products obtained depends greatly on the purity of the original cellulose fibre, its moisture-content, whether it consists of cellulose or hydrated celluloses ("hydrocelluloses" produced by preliminary maceration with dilute mineral



acid), and the manner and order in which it is mixed with the acetylating agents.

The cotton or other fibre is first of all degreased by treatment with petrol or benzol, and may then be partially hydrated by steeping in dilute sulphuric acid,<sup>13</sup> although, whilst facilitating acetylation, this weakens the fibre to some extent. Finally it is dried as thoroughly as possible (to a moisture content not exceeding 2-3 per cent.).

Two examples from patent literature may be given to illustrate the influence of conditions of acetylation on the product obtained.

(a) <sup>14</sup> A mixture of 270-310 parts of acetic anhydride, 390-410 parts of acetic acid, and 5-8 parts of sulphuric acid is added to 100 parts of cellulose with good stirring and cooling so that the temperature does not rise above 40°, although finally it is raised to about 55°. The action is continued until the product is completely soluble in chloroform, when it is precipitated with water, freed from acetic acid, and then consists mainly of the triacetate of cellulose.

(b) <sup>15</sup> One hundred parts of cellulose are added to a mixture of 800 parts of glacial acetic acid, 200-350 parts of acetic anhydride, and 15-20 parts of sulphuric acid maintained at 0°. The acetylation is carried out at a low temperature and requires about three to six hours, the temperature being allowed to rise to 30° towards the end of the period. The greater proportion of acetic acid present is stated to retard undue disruption of the cellulose structure and result in products of greater viscosity and tensile strength.

In nearly all processes for acetylation of cellulose the catalyst employed is sulphuric acid; hydrochloric acid has also been proposed, but does not appear to be so useful as the former acid, whilst zinc chloride is recommended as an acetylating catalyst on the score that its action is more regular and less disruptive than that of sulphuric acid.

It will be noticed that, from the catalytic standpoint,

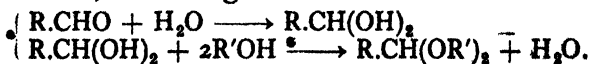
technical experience in the acetylcellulose industry is broadly similar to that in the manufacture of esters, the cheap and convenient sulphuric acid being employed under appropriate conditions whenever possible, whilst for special cases other catalysts (in this instance zinc chloride) are used.

*Acetals*.—The acetals,  $R.CH(OR')_2$ , are mixed ethers derived from an alcohol and the aldehydrol form of an aldehyde,  $R.CH(OH)_2$ ; in one or two instances they are of therapeutic value and are manufactured by condensation methods which involve homogeneous catalysis similar to that dealt with in the production of esters.

*Methylal*,  $CH_2(OCH_3)_2$ , (b.p.  $42^\circ$ ), the dimethyl ether of formaldehyde, is used as an anæsthetic and is produced by heating 2 parts of paraformaldehyde with 5 parts of a 1 per cent. solution of hydrogen chloride in methyl alcohol at  $40^\circ$ – $50^\circ$  under a reflux condenser for some hours. After standing for some time and cooling, sufficient lime is added to neutralise the mineral acid and the liquid is fractionated.

*Acetal*,  $CH_3.CH(OC_2H_5)_2$ , (b.p.  $104^\circ$ ), is the corresponding diethyl ether of acetaldehyde, and is produced from acetaldehyde and alcohol by the above method or by treating a mixture of acetaldehyde and alcohol with about 10 per cent. of its weight of calcium or similar chloride in presence of a small amount of hydrochloric acid under a reflux condenser.<sup>16</sup>

The action of hydrochloric acid or calcium chloride in the formation of acetals is essentially one of catalytic dehydration, according to the scheme

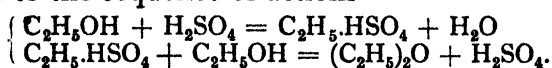


• *Ethers*.—A very important type of catalytic dehydration in the liquid state is the removal of the elements of water from two molecules of an alcohol, forming the corresponding ether. •

*Ethyl Ether*,  $(C_2H_5)_2O$ , is, of course, used in very large quantities in surgery as an anæsthetic, and in

chemical work and in fine chemical manufactures as a solvent: It was also required extensively during the war of 1914-1918 in the manufacture of propellant explosives, when it was found that a mixture of ether and alcohol was a serviceable substitute for acetone as a solvent for nitro-cellulose and nitroglycerine. A similar mixture, under the name of Natalite, has been found useful as a fuel for motors, and is capable of being used in engines designed for the combustion of petrol.

For industrial purposes, ether has always been produced by the catalytic action of sulphuric acid on alcohol, known and represented for years past as due to the sequence of actions



By reason of this procedure, the anæsthetic is frequently sold as "sulphuric ether," whilst the equally familiar "methylated ether" is the product from methylated or denatured alcohol, and contains a small proportion of methylethyl ether and possibly dissolved dimethyl ether.

Prior to the war period the production of ether was effected by a discontinuous process: four parts of alcohol and three parts of sulphuric acid were heated in a lead-lined still to about  $140^\circ$ , when ether commenced to be formed and a distillate of ether mixed with alcohol was collected. Further quantities of alcohol were added to the still to replace the distillate until the amount of water retained by the sulphuric acid was great enough to retard the dehydration. The remaining alcohol and ether were then distilled off and the ether and alcohol separated by fractionation, the recovered alcohol being collected and used with a fresh charge of sulphuric acid. Senderens<sup>17</sup> showed that, as in the case of esterification (*cf.* p. 407), the process could be increased in efficiency and conducted at a lower temperature (about  $120^\circ$ - $130^\circ$ ) if a small percentage of anhydrous aluminium sulphate

were added to the still-charge. Nevertheless the discontinuous process involved considerable losses of alcohol as well as of sulphuric acid, and was also wasteful from the point of view of heat consumption.

For the production of ether for ether-alcohol mixtures in explosives and internal combustion engine fuel, a continuous process was devised by Barbet,<sup>18</sup> the first English installation being at H.M. Factory, Gretna. The plant consists essentially of the following parts :--

(i.) An alcohol vaporiser, comprising a steel vessel fitted with vertical steel tubes ;

(ii.) The reaction still, constructed of lead-lined steel ;

(iii.) A continuous fractionating and rectifying column, built in copper and made up of two sections, the lower one serving to recover unchanged alcohol and containing twenty-two fractionating plates, whilst the upper one (one-third the height of the former and somewhat narrower) is designed to rectify the ether. The two parts of the column are separated by a solid plate, and vapour from the top of the lower column passes to the lowest plate of the upper part through an intermediate condenser, which returns a continuous stream of alcohol to the top plate of the lower column. Alcohol is recovered from a plate near the top of the lower column and ether is similarly withdrawn from the top plates of the upper section and, to a certain extent, by condensation of the vapours in condensers attached to the head of the column.

In starting up the process a mixture of one volume of 78 per cent. sulphuric acid and two volumes of 92 per cent. alcohol is charged into the still and heated, whilst alcohol is fed into the alcohol vaporiser and, when the contents of the still are at  $105^{\circ}$ , is admitted in the state of vapour into the still. The temperature of the latter is increased, and finally, as the reaction increases, steam is shut off and the temperature of reaction ( $128^{\circ}$ ) maintained by the heat evolved,

sufficient alcohol vapour being blown into the acid mixture to maintain it at about this point. The process is thereafter continuous, and the plant will run for long periods before it is necessary to use fresh acid.

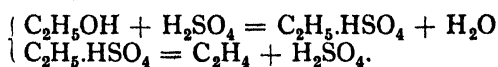
The vapours from the still pass through a 2 per cent. solution of caustic soda in a scrubber, and thence into the lower fractionating column (about half-way up). This column is supplied with live steam at its base and is so controlled that the effluent at this point does not contain any alcohol. The mixture of ether and alcohol is driven up the column by the steam as indicated above and separated into its components, anhydrous alcohol containing a small percentage of ether being withdrawn from the top of the lower column and pure ether separated at the top of the upper column.

A unit capable of producing 25 tons per 24-hour day gave an overall efficiency (yield) of ether of over 94 per cent. on a continuous production of 5,000 tons, the materials consumed per ton of ether being 1.43 tons of 92 per cent. alcohol, 0.0012 tons of 100 per cent. sulphuric acid, and 0.0014 tons of caustic soda. The weight of steam used varied between 6,000 and 10,000 lb. per ton of ether, according to whether fresh or recovered alcohol was used in the still. The efficiency and smoothness of this continuous system of ether production renders it an excellent example of the possibilities of catalysis in industrial organic chemistry, and for this reason the Barbet process has been described at considerable length.

*Ethylene.*—The trend of economic factors seems to lie in the direction of converting ethylene into alcohol (cf. this Section, Chapter I., p. 387) rather than to demand the production of ethylene from alcohol, but it sometimes happens that the hydrocarbon is required. Dehydration of alcohol with production of ethylene can be effected catalytically by several means; the

passage of heated alcohol vapour over appropriate solid catalysts has been dealt with in Section II. (Chapter X., p. 256), but older methods consist in catalytic dehydration in a homogeneous liquid system by means of sulphuric or phosphoric acid.

If, in the process described above for the discontinuous preparation of ether, the temperature of the charge in the still is raised to about  $160^{\circ}$ – $170^{\circ}$  and the proportion of alcohol reduced, ethylene is produced instead of ether :—

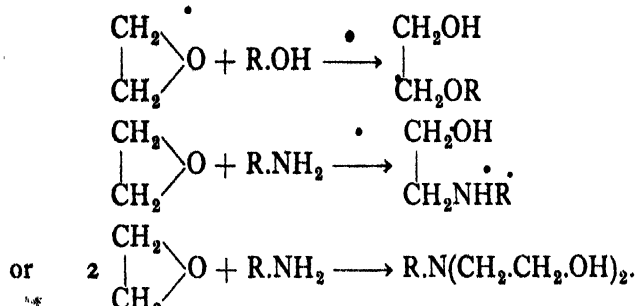


For ethylene production the ratio of alcohol to concentrated sulphuric acid in the still is kept at about one of alcohol to two of acid (by volume); as in the case of ether, the action proceeds more rapidly and readily if the charge contains 5 per cent. of anhydrous aluminium sulphate : at  $157^{\circ}$  the evolution of ethylene is more than twelve times as rapid in presence of the aluminium salt as when sulphuric acid only is used.

The use of sulphuric acid at the necessary temperature leads to a certain amount of carbonisation with concurrent production of sulphur dioxide, and, especially for relatively small outputs of ethylene, it is more economical and convenient to employ phosphoric acid. For this purpose metaphosphoric acid ("syrupy phosphoric acid") is charged into a lead-lined still, connected with a condenser or scrubber followed by a gas-holder for the ethylene, and is heated to about  $150^{\circ}$ , when alcohol is slowly added so that a steady and continuous evolution of ethylene takes place. In this way a more or less continuous production of relatively pure ethylene is secured.

*Glycol Ethers, etc.*—An interesting case of catalysis (which really belongs to the heterogeneous section) is the condensation of ethylene or propylene oxide with alcohols, phenols or amines in presence of an acid-activated hydrosilicate (fuller's earth). Such materials, known technically as tonsil, acsil, etc., are slightly

acidic in reaction ( $p_K$  2.3-3). When ethylene oxide is passed into a boiling solution of ethyl alcohol containing in suspension an acid hydrosilicate of this type, glycol ethyl ether is produced in 80 per cent. yield.<sup>19</sup> The general reactions involved are:—



The important  $\beta$ -chloroethyl ether of glycol,  $\text{CH}_2(\text{OH}).\text{CH}_2.\text{O}.\text{CH}_2.\text{CH}_2\text{Cl}$ , can be similarly prepared from ethylene oxide and ethylene chlorhydrin.





## CHAPTER IV

### EXAMPLES OF OTHER HOMOGENEOUS CATALYTIC ACTIONS EMPLOYED IN ORGANIC CHEMICAL INDUSTRIES

THE types of homogeneous catalysis which have so far been described fall in some measure into a series of connected stories, but there is left a wider number of processes, in common use in the dyestuffs and other organic chemical industries, which depend upon catalytic action for their efficiency; in practically all these cases, also, the application of catalysts has grown up more or less fortuitously and rests on isolated discoveries which, however logically developed in their later stages, were by no means the result of any definite attempt to apply catalysis to the processes in question.

Consequently systematic treatment of this diffuse field is extraordinarily difficult, whilst it is impossible to discuss at length in this volume the technical procedure involved in any given case. Nevertheless, in the glamour of modern thermodynamical treatment of catalysis and the splendour of the recent developments in the fields of high-pressure catalytic synthesis, fat and naphthalene hydrogenation, the catalytic syntheses from acetylene, and so on, it is apt to be overlooked that for upwards of half a century catalytic processes have been widely used as a matter of course in the technical chemistry of the aromatic derivatives. The reason for this may lie in the frequent comparative obscurity of the function of the catalyst, or in the fact that the latter magic word was not so familiar when many of these processes were in their infancy. However this may be, it seems reasonable in a treatise on industrial catalysis to attempt a review of these older forms of catalytic action, even though this is confined

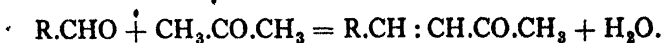
almost to a bare enumeration of a large number of somewhat diverse chemical actions.

Since most of the actions under consideration are conducted in a homogeneous liquid condition, it is convenient to deal with them in this chapter, including, at the same time, a minority of similar processes which may, strictly speaking, involve catalysis at a solid surface, and therefore may belong more correctly to one or other of the chapters of Section II. It is only possible to indicate the scope of this part of the subject by reference to a few general cases selected from the many which are available; these are classified under the general headings of the types of organic reaction to which they belong. The applications of catalysis in the technical polymerisation of organic compounds are reviewed in the concluding chapter of this Section (Chapter V.).

#### (a) Actions of Condensation.

One or two cases, which resemble those discussed in the last chapter in that the actions involve the elimination of the elements of water from two molecules of organic compounds, will first receive mention.

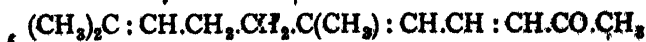
A very useful synthetic laboratory process, which also has some industrial importance, is the condensation of an aldehyde or ketone with acetone according to the scheme



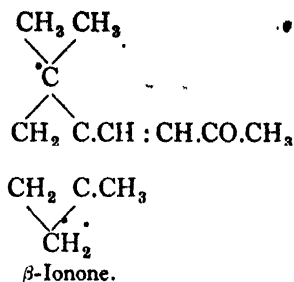
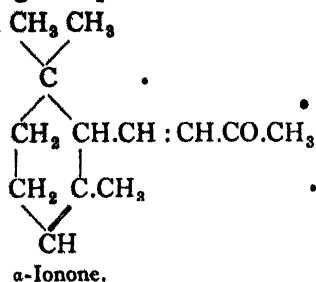
This proceeds, as originally shown by Claisen,<sup>1</sup> in a dilute alkaline medium, the action of the alkali being catalytic.

The resulting unsaturated ketones have, as a rule, no technical interest, but in some cases they are convertible into derivatives of industrial value.

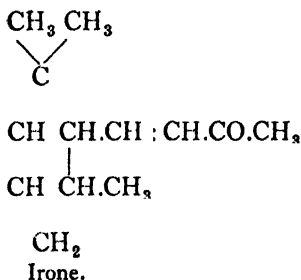
Thus, Tiemann and Krüger<sup>2</sup> found that baryta solution caused citral to condense with acetone to give the compound *pseudo-ionone*



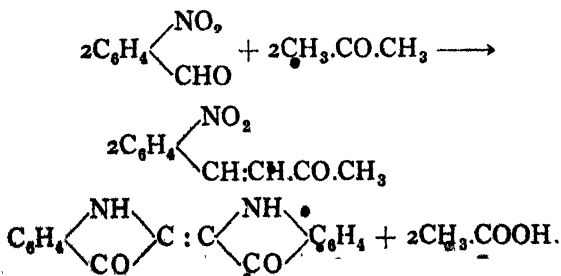
which, by the further catalytic action of dilute sulphuric acid, is rearranged into a mixture of isomeric ring-compounds, the *ionones* :—



These are produced in large quantities for the sake of their perfume, which closely resembles that of violets or orris, due, in the latter case, to the presence of yet another ketone isomeric with the ionones, namely,



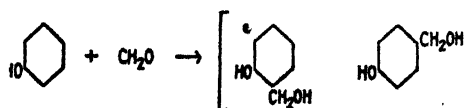
Again, in Baeyer and Drewsen's<sup>3</sup> process for the manufacture of synthetic indigo, *o*-nitrobenzaldehyde is similarly condensed with acetone by means of dilute caustic soda, further rearrangement leading to the formation of indigo :—



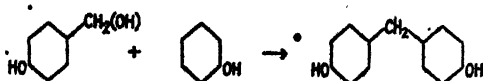
**Condensation Resins.**—The very large industry of plastics, moulded products and lacquers, based on resins of the bakelite type, depends on the controlled condensation of phenols, urea and other substances with formaldehyde and other aldehydes in the presence of basic, or in some cases acidic, catalysts. In 1934, the world production of synthetic resins was in the neighbourhood of 70,000 tons, 75 per cent. of which were condensation resins involving formaldehyde or its derivatives. It is hardly necessary to stress the many uses to which these materials are put in modern industry.

The phenol-formaldehyde condensation is capable of two main variations.<sup>4</sup> If less than one equivalent of formalin is condensed with one equivalent of phenol in the presence of an acid catalyst, a permanently soluble and fusible resin of the "Novolak" type results. If, however, rather more than one equivalent of formalin is employed, in the presence of alkalies, a fusible and soluble resin (bakelite "A" or a resol) is produced, which by moderate heat treatment is converted into a "resitol" or bakelite "B" (infusible, but softens on heating and swells in organic solvents). Further heating converts the latter product into a hard, completely insoluble and infusible material known as a "resite," or bakelite "C," which forms the basis of the familiar moulded articles.

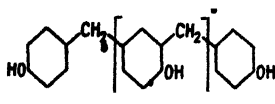
The mechanism of the phenol-formaldehyde condensation is considered to be as follows.<sup>5</sup> Initial reaction of phenol and formaldehyde leads to the formation of *o*- and *p*-hydroxy-benzyl alcohols :—



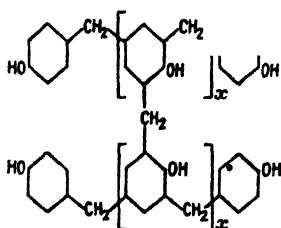
Further addition of phenol produces dihydroxydiphenyl methanes (of which there are three possible isomers). For example :—



By further condensation, long chain compounds such as



can be built up, existing in many isomeric forms. The soluble, fusible Novolak resins are considered to possess this structure. In the preparation of heat-hardening resins the presence of excess of methylene groups leads to cross-linking of these chains and the formation of highly complex isomers of the type :—



The resinous nature of the products is due to the presence of a mixture of highly complex compounds which mutually restrain tendency towards crystallisation.

The original process of bakelite manufacture was somewhat as follows <sup>6</sup> :—

Phenol or cresol and an equal volume of commercial formalin were heated in the presence of not more than 20 per cent. of catalyst (ammonia, caustic soda, alkali sulphites or other substances), and the viscous product separated from the aqueous mixture. The crude product was heated by steam to thicken it slightly and to drive off water, and at this stage, various fillers, such as asbestos, wood fibre, rubber, barium sulphate, graphite, etc., or “modifiers” such as resins or nitrocellulose, were added. On heating the product under pressure at 110°-140° a hard, compact,

moulded material resulted after 1-2 hours (in modern practice the moulding and hardening time is considerably reduced).

Ammonia is the catalyst most usually employed, and it is frequently added in the form of hexamethylene tetramine. The aqueous formalin can in fact be entirely replaced by this substance with the advantage that water is eliminated from the system.<sup>7</sup> Hexamethylene tetramine, however, is most valuable as a hardening agent in the conversion of the initial products to the bakelite "C" stage, a process which involves the reaction of further methylene groups. Soluble and fusible Novolak resins can be hardened by condensation with 5 per cent. of hexamethylene tetramine.<sup>8</sup>

In the preparation of the Novolak resins, hydrochloric acid is the usual catalyst employed,<sup>9</sup> although for the production of resins of maximum colour stability, phosphoric acid has been recommended.<sup>10</sup>

Resins of various types and properties have been prepared by the condensation of a wide variety of phenolic compounds with formaldehyde. Higher phenols, such as the xylenols, produce resins which have the property of solubility in vegetable oils and hence are of value for varnish manufacture.<sup>11</sup> Flexible gramophone records and talking-film discs can be prepared by coating paper with a resin produced from resorcinol and formaldehyde.<sup>12</sup> Acetone or methyl ethyl ketone, when condensed with formalin in the presence of mild alkalies such as barium hydroxide, yield products which polymerise to clear, glass-like bodies.<sup>13</sup>

Similarly, formaldehyde has been replaced by acetaldehyde, butaldehyde, benzaldehyde, furfural, carbohydrates, acrolein, and many other compounds, either for reasons of cost or for producing resins of specific properties.

Apart from the phenol-formaldehyde resins, those derived from urea and formaldehyde are the most

important. Of particular value is the glass-like transparency of the moulded products, which confers a depth and brilliancy of colour impossible with the phenol resins. In view of the potential supplies of urea (from ammonia and carbon dioxide) an almost unlimited source of such resins exists. Owing to the transparent appearance of these products many claims have been made for them as organic glasses. In practice, however, the material tends to crack and develop fissures owing to a continuance of the condensation process, and in humid atmospheres absorption of water tends to dim the transparency. The usual practice of incorporating 30-40 per cent. of cellulose fibre filler overcomes these disadvantages, but of course destroys the transparency and produces a translucent effect.

Formaldehyde and urea may be condensed directly in the presence of an acid or alkaline catalyst (more usually the former), but it is frequently found preferable first to prepare the methyl or dimethyl urea by condensation of urea and formaldehyde in alcoholic solution in the presence of alkali. The methyl ureas can then be rapidly converted into glass-like products by heating them with, for example, 0.3 per cent. of chloracetic acid.<sup>14</sup> A laminated material, said to be suitable as a glass substitute in windscreens, can be prepared by employing the resin in two stages of condensation, the less condensed stage serving as an adhesive for sheets of the more highly condensed stage.<sup>15</sup> Apart from moulded products, organic glasses, and other similar forms, urea resins have been used as a treatment for textiles to confer crease-resisting properties, in the production of special adhesives, and in a variety of other ways. Owing to the water-resisting properties which it confers upon the products, thiourea has been claimed as an important substitute for urea, but its tendency to stain the steel moulds used in the industry, and the slow rate of "cure" of the products have mitigated against its

widespread use; mixtures of urea and thiourea have been found more satisfactory.

The number and variety of starting components, catalysts and methods of condensation in use or suggested for the manufacture of synthetic resins and plastics have become so vast in recent years that it is impossible to go into the subject in any detail. For such information the interested reader is referred to a monograph such as that of Carleton Ellis, "The Chemistry of the Synthetic Resins," Vols. I and II, Reinhold Pub. Corp., U.S.A., 1935.

*Friedel and Crafts Reaction.*—The next class of condensations to which we shall refer are those in which hydrochloric acid is eliminated from two organic molecules by the classical aluminium chloride method of Friedel and Crafts.<sup>16</sup> This is of especial interest because it is one of the few of the older organic catalyses which have been studied with reference to reaction-mechanism. It is also an instance in which the intermediate complex between catalyst and either interactant is sufficiently stable to be isolated: crystalline derivatives of the form  $(\text{RCl}, \text{AlCl}_3)_2$  have been isolated in the case of acid chlorides, and double compounds such as  $(\text{C}_6\text{H}_5, \text{AlCl}_3)_2$  from hydrocarbons and aluminium chloride. In a thorough study of the interaction of toluene and benzyl chloride in presence of anhydrous aluminium or ferric chlorides, Steele<sup>17</sup> found in 1903 that a short period of induction marked the formation of the intermediate derivative, after which, broadly speaking, the action proceeded according to the unimolecular law and declined in speed as the concentration of organic halogen compound diminished; after a time the influence of a complex made up of the product and the catalyst served as an additional retardation. It appears that Steele's results form a close analogy to the views developed some fifteen years later, when very similar deductions were made with regard to the probable mechanism of the addition of hydrogen to



unsaturated liquid organic compounds in presence of nickel.

It follows that, if the Friedel and Crafts reaction depends on the production of intermediate complexes between aluminium chloride and each of the inter-actants, the halogens in a mixture of two organic halides should be partially interchanged in presence of this catalyst. Dougherty<sup>18</sup> has found this to occur: for instance, equimolecular mixtures of methyl iodide and ethyl bromide gave on treatment with aluminium chloride a mixture containing, in addition, methyl bromide and ethyl iodide; ethylene chlorobromide similarly yielded a mixture containing 50 per cent. of the original compound with ethylene dichloride and ethylene dibromide, and the same equilibrium mixture resulted, starting from a mixture of ethylene dichloride and dibromide; ethyl bromide and chloroform gave a mixture containing 35 per cent. of dichlorobromomethane.

The activity of aluminium (or ferric) chloride is considerably affected by the presence of adsorbed hydrogen chloride. Aluminium chloride made from the metal and hydrochloric acid may contain as much as 9 c.c. per gram of adsorbed hydrogen chloride, and the latter, according to Boswell and McLaughlin,<sup>19</sup> is not removable by a current of inert gas at the ordinary temperature; repeated sublimation in nitrogen reduces the content of adsorbed gas and much improves the activity of the aluminium chloride. Bodendorf<sup>20</sup> recommends that the latter be prepared by passage of dry hydrogen chloride through boiling benzene, toluene or xylene containing aluminium powder in suspension (together with small amounts of mercuric chloride and iodine as catalysts).

Boswell and McLaughlin,<sup>19</sup> and also Galloway and Whitby,<sup>21</sup> point out that, although ferric chloride is much less active than aluminium chloride, an equimolecular mixture of the two chlorides has an activity greater than the sum of the activities of the separate

components. Riddell and Noller<sup>22</sup> found that the yield of product with aluminium chloride alone is proportional to the amount of the latter employed up to an optimum quantity (1 mol. for acid chlorides and 2 mols. for acid anhydrides); with mixtures of aluminium and ferric chlorides, they distinguished two types of reactions, namely, those in which the yield decreases proportionately with the amount of ferric chloride present (*e.g.*, acid chlorides and benzene), and those in which the yield first falls, then rises to a maximum at about equimolecular proportions of the two chlorides, and then decreases to the yield obtained with ferric chloride alone (*e.g.*, acid anhydrides or sulphonic chlorides and benzene). This is thus an extension of the conclusions of Gallay and Whitby,<sup>21</sup> who were studying the condensation of phthalic anhydride with benzene. Martin *et al.*<sup>23</sup> have recently made a similar study of the production of phenyltolylketone from toluene and benzoyl chloride which confirms both the earlier views of Steele<sup>17</sup> on the mechanism of the Friedel and Crafts condensation and the observations of the above authors with regard to the optimum effect of an equimolecular mixture of ferric and aluminium chlorides; they observed, however, a continuous increase in activity as a result of admixture of ferric chloride up to the maximum, and their results appear dissimilar from those of Riddell and Noller<sup>22</sup> in that the action studied (condensation of an acid chloride and an aromatic hydrocarbon) falls in the category in which, according to the latter, ferric chloride progressively reduces the yield obtained with aluminium chloride alone.

Wertyporoch *et al.*<sup>24</sup> have found further support for Steele's views of ternary complex formation by measurements of the electrical conductivities and transport numbers of solutions of anhydrous ferric chloride in various alkyl and acyl chlorides, together with the alteration in these properties following addition of benzene and other aromatic hydrocarbon derivatives.

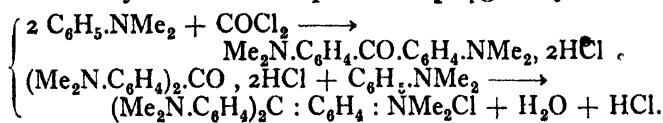
They state that beryllium and zirconium chlorides have a slight condensing action, but that mercury, thallium, thorium, titanium or tin chlorides do not behave as Friedel and Crafts catalysts even at increased temperatures and pressures.

The application of the Friedel-Crafts synthesis in industry is widespread; a cursory indication of some of the variants may be given. An interesting suggestion for the production of toluene from benzene is due to Sifton,<sup>25</sup> who employs iron turnings in admixture with anhydrous aluminium chloride. Hydrogen chloride (mainly derived from that subsequently expelled in the synthesis) is dried and passed through stills containing methyl alcohol and anhydrous zinc chloride, when gaseous methyl chloride is produced, freed from contained methyl alcohol in condensers, and passed up a series of plate-columns. The plates contain layers of the catalyst over which benzene circulates in a downward direction, the columns being maintained at  $45^{\circ}$ – $55^{\circ}$ . The plant is operated on the counter-current system, so that the fresh methyl chloride enters a column in which the benzene is already nearly converted into toluene and emerges through one containing almost fresh benzene.

An important use of the method is in the industrial production of anthraquinone and its derivatives from phthalic anhydride and a benzenoid hydrocarbon. In the United States, according to Downs,<sup>26</sup> anthraquinone is chiefly manufactured by condensing phthalic anhydride with benzene in presence of aluminium chloride and subsequently further condensing the *o*-benzoylbenzoic acid thus produced to anthraquinone by concentrated sulphuric acid. Methyl- and chloro-anthraquinones are similarly produced, starting respectively from toluene or chlorobenzene and phthalic anhydride. Groggins and Newton<sup>27</sup> have described in detail the similar technical preparation of 1 : 2-benzanthraquinone or its sulphonic acids from naphthalene and phthalic anhydride. The

latter (in equimolecular proportions) are condensed (to give a 97.5 per cent. yield of  $\alpha$ -naphthoylbenzoic acid) in solution in 3 parts of *o*-dichlorobenzene in presence of a 10 per cent. excess of aluminium chloride at  $0^\circ$ . The solvent is recovered by distillation in steam and the product condensed to benzantraquinone by heating for seven hours at  $80^\circ$  with 6 parts of 95 per cent. sulphuric acid; sulphonation takes place simultaneously, but can be prevented by adding a weight of boric acid equal to that of the  $\alpha$ -naphthoylbenzoic acid. Use of less sulphuric acid results in incomplete ring-closure, while higher acid ratios increase the amount of sulphonation.

The synthesis is also applied technically in the preparation of aromatic ketones and allied derivatives, and very frequently the organic halide consists of carbonyl chloride,  $\text{COCl}_2$ . Thus, when 40 parts of dimethylaniline and 6 parts of carbonyl chloride are maintained at  $20^\circ$ – $30^\circ$  for some hours in presence of 10 parts of aluminium (or ferric) chloride the dyestuff Crystal Violet is produced in good yield <sup>28</sup> :—



The interaction of phenols and arylamines with carbon dioxide in presence of aluminium, ferric or zinc chlorides at high pressures (40–150 atmospheres) and temperatures of  $100^\circ$ – $200^\circ$  has been extensively investigated by Morgan and Pratt <sup>29</sup> at the National Chemical Laboratory at Teddington. Phenol, which with carbon dioxide at  $100^\circ$  and 90 atmospheres yields salicylic acid, gives 4:4'-dihydroxybenzophenone at  $105^\circ$ – $110^\circ$  and 70 atmospheres, and diphenylether at  $200^\circ$  and 120 atmospheres; dimethylaniline gives *p*-dimethylaminobenzoic acid with zinc chloride at  $150^\circ$  and 70 atmospheres, and Michler's ketone,  $\text{Me}_2\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2$ , with aluminium chloride at  $150^\circ$  and 65 atmospheres; anilines and carbon

dioxide at 130° and 60 atmospheres yield carbanilides. Many other similar instances are recorded in Morgan and Pratt's paper.

The condensation of *olefines* with benzenoid hydrocarbons by means of aluminium chloride is an instance of the Friedel and Crafts change which has some technical importance. Reid<sup>30</sup> and his colleagues have examined the interaction in this way of ethylene or propylene with benzene, toluene or naphthalene, and find that the condensation proceeds more readily than if the corresponding alkyl chlorides are employed. The reaction cannot in general be controlled to give a single product. For instance, ethylene and benzene give a mixture in which triethylbenzenes usually predominate, but mono- and di-ethylbenzenes are also formed, and the reaction can be continued until hexa-ethylbenzene is produced. Propylene and benzene react less vigorously in presence of aluminium chloride, the main products being di- and tri-*isopropyl*benzenes, and the action not proceeding beyond tetra-*isopropyl*benzenes. This process has recently been applied to the production of alkylaryl hydrocarbons<sup>31</sup> with high anti-knock ratings by first treating benzene hydrocarbons with gaseous olefines from petroleum gases in presence of sulphuric acid, and then condensing the products with more benzene or other aromatic hydrocarbon in presence of aluminium chloride. A somewhat analogous and equally important case is the conversion of certain olefinic hydrocarbons produced from water-gas by the Fischer-Tropsch process (Section II., Chapter III., p. 115) into useful lubricating oils, either by auto-condensation in presence of aluminium chloride, or by first chlorinating these fractions and then subjecting them to the Friedel and Crafts' condensation, either alone or together with commercial xylene or other aromatic hydrocarbon.<sup>32</sup>

It should be noted that Ipatiev *et al.*<sup>33</sup> have shown that alkylation of aromatic hydrocarbons by the lower olefines can be effected by means of sulphuric or

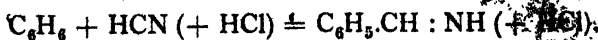
phosphoric acids as well as by aluminium chloride. With sulphuric acid in the cold, alkylation frequently takes place readily, but may be accompanied by formation of di-alkyl sulphates and (with *iso*-butene and higher olefines) by polymerisation (*e.g.*, to di- or tri-*isobutene*). To some extent the course of the reaction can be controlled by sulphuric acid of a precisely chosen degree of concentration (hydration). When di- or tri-*isobutene* reacts with benzene in presence of 96 per cent. sulphuric acid or of aluminium chloride, depolymerisation followed by alkyl-(butyl)-ation of the benzene to mono-, di- and tri-butylbenzenes takes place. In presence of phosphoric acid, alkylation of aromatic hydrocarbons is effected at high temperatures under pressure.

Finally, reference should be made to the condensation in presence of aluminium chloride of alkylene oxides <sup>34</sup> with aliphatic, aromatic or heterocyclic derivatives; benzene and ethylene oxide yield phenyl-ethyl alcohol, *n*-pentane and ethylene oxide give *n*-heptyl alcohol (other paraffin hydrocarbons behaving similarly), while ethylene oxide and pyridine or naphthalene derivatives furnish respectively  $\beta$ -hydroxy-ethylpyridines and  $\beta$ -hydroxyethylnaphthalenes.

*Gattermann Reaction*.—A nearly related process to the last is the Gattermann synthesis <sup>35</sup> of aldehydes from carbon monoxide, hydrogen chloride and an aromatic hydrocarbon in presence of aluminium chloride containing about 10 per cent. of cuprous chloride; the mixed gases are passed through dry benzene containing a considerable proportion of the catalyst at about 40°, when the following action occurs:—



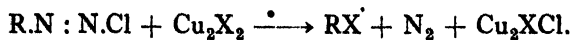
Hoesch improved this process subsequently by substituting hydrocyanic acid for the carbon monoxide:



the imino-aldehyde being readily converted into the

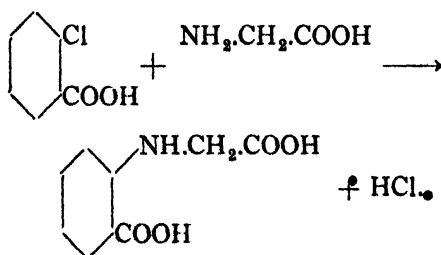
aldehyde by the action of water; this modification has been found useful in technical practice, especially in the production of aldehydic derivatives of phenolic ethers.

Cuprous chloride and other cuprous salts have also proved serviceable in the conversion of aromatic diazo-compounds into chloro-, bromo-, or other derivatives by the well-known Sandmeyer reaction <sup>36</sup> :—



Gattermann's modification <sup>37</sup> of this process, in which finely-divided metallic copper is used in place of the cuprous halide, may be a case of heterogeneous catalysis, or the change may be effected in reality by traces of cuprous salt produced in the reaction medium from the metal.

The Gattermann copper catalyst also effectively promotes the elimination of hydrogen chloride between a chlorophenyl residue and an amino-group in some cases; for example, in an important stage of one form of the phenylglycine indigo synthesis <sup>38</sup> :—



It is similarly useful in the production of nitrapiline derivatives by the action of ammonia on chloro-derivatives of nitrated hydrocarbons.

The actual catalyst in reactions of this kind may be an alcohol-soluble compound of copper with the amino-derivative. <sup>39</sup>

Considerable interest has been shown, especially in the United States, in the possibility of manufacturing aniline and phenol from benzene *via* monochloro-

benzene. These reactions can be effected if chlorobenzene is heated at a high temperature and pressure with, respectively, ammonia solution or caustic soda solution. The "ammonolysis" process, as it has been called, was originally carried out by autoclaving chlorobenzene with concentrated ammonia in presence of copper salts or reduced copper. Thus, an early patent<sup>40</sup> of 1908 states that an 80 per cent. yield of aniline is obtained by heating chlorobenzene with excess of aqueous ammonia and copper sulphate at  $180^{\circ}$ – $200^{\circ}$ . Results of later investigations with the aid of modern high-pressure technique suggest that the need for the copper catalyst has been exaggerated. Groggins,<sup>41</sup> in a survey of various processes of this kind, including aniline from chlorobenzene and  $\beta$ -naphthylamine from  $\beta$ -naphthol, argues that the use of copper salts can be limited to the production of volatile amines, but points out that efficient mixing of the aqueous and organic liquids is essential; mechanical agitation is required, and may be supplemented by the use of nitrobenzene, amyl alcohol, or other substance as a common solvent for the interactants. Excess of ammonia minimises the formation of imino-compounds or of phenols as by-products.

The corresponding hydrolysis of chlorobenzene to phenol by 10 per cent. caustic soda solution at  $300^{\circ}$  was patented by Meyer and Bergius<sup>42</sup> in 1913, following earlier proposals by F. Bayer and others<sup>43</sup> to carry out the same process in presence of metallic copper. The reaction received renewed attention from 1917 onwards in America, and a resumé of the chief results was given by Hale and Britton<sup>44</sup> in 1928. These authors state that chlorobenzene is hydrolysed by aqueous alkalis at  $340^{\circ}$ – $370^{\circ}$  with production of phenol in good yield; 6–10 per cent. of diphenyl ether may, however, occur as a by-product. The effect of copper or copper salts is only marked at lower temperatures. The optimum concentration of sodium hydroxide was about an 8 per cent. solution, but



sodium carbonate solution effects the hydrolysis just as well as caustic soda, and if the carbonate is used, subsequent acidification of the sodium phenate solution can be avoided. Benzenesulphonic acid and caustic soda solution undergo a similar change at and above  $300^{\circ}$ , and the economic value of the process seems to depend on whether the conversion of benzene into chlorobenzene is cheaper than its sulphonation to benzenesulphonic acid.

The chief interest of these high-pressure methods for the production of anilines and phenols is that they involve the utilisation of chlorobenzenes as the intermediate compound in place respectively of nitrobenzenes or benzenesulphonic acids.

(b) Formation of Hydrocarbon Halides by Substitution or Addition.

Technical chlorinations are frequently facilitated by the presence of metallic or other chlorides which act as "chlorine carriers" or catalysts. Some of the more important applications of these catalysts are as follows :—

(i.) Benzene and toluene are converted into chloro-derivatives by passing a current of dry chlorine gas into the hydrocarbon, which contains in suspension either anhydrous ferric chloride, or a mixture of the latter with reduced iron powder (equivalent to ferrous chloride or subchloride).<sup>45</sup> The combined action of 1 per cent. of iron and 0.1 per cent. iodine is said <sup>46</sup> to be extraordinarily effective in the chlorination of benzene and of its derivatives.

(ii.) For chlorination of the aliphatic radical in an aromatic hydrocarbon, for example, in the production of benzyl and benzal chloride from toluene, phosphorus trichloride is a useful catalyst, and probably sulphur chloride is also efficient. The action in this case is carried out at the boiling point of the liquid mixture in presence of 1–3 per cent. of phosphorus trichloride ; the main product is the monochlorinated

derivative (benzyl chloride) unless the action of the chlorine is very prolonged or carried out in strong ultra-violet light.

.(iii.) Similarly, substitution of hydrogen by chlorine in the methyl radical of acetic acid is facilitated by the presence of small quantities of sulphur or phosphorus (Russanoff).<sup>47</sup> Monochloroacetic acid is produced by passing chlorine gas into boiling glacial acetic acid containing about 1 per cent. of finely-divided sulphur for some hours.; chlorides of sulphur are formed initially and chlorination then proceeds steadily and almost quantitatively. The reaction appears to be autocatalytic, since chlorination of acetic acid proceeds readily if a little monochloroacetic acid is added, in the absence of sulphur or other catalyst.<sup>48</sup>

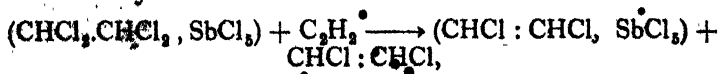
(iv.) Chlorination of the simpler paraffin hydrocarbons is of some technical importance. The chlorination of methane in presence of partly reduced cupric chloride on pumice has been studied by Boswell and McLaughlin,<sup>49</sup> who found that the process could be controlled by dilution of the methane-chlorine mixtures with varying proportions of nitrogen. With nitrogen, methane and chlorine in the ratios 70 : 7 : 1, the moist gases at 450° gave a 75-80 per cent. yield of methyl chloride; in the ratio 7 : 1 : 4 at the same temperature, methane was converted into carbon tetrachloride in 80 per cent. yield. Ethyl chloride was similarly produced from ethane.

The most interesting recent work in this field deals with the chlorination of the pentanes and butanes present in natural gas from American petroleum. The chloro-derivatives are, of course, the intermediates in the conversion of these lower paraffins into the corresponding alcohols, and this process is an alternative route to the same alcohols as those which are obtained by hydration of corresponding olefine constituents of the natural gas (*cf.* this Section, Chapter I., p. 388). Ayres<sup>50</sup> states that, in 1929, 100,000 gallons per day of pentanes were chlorinated by the Standard

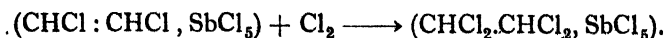
Oil Company. The most effective conditions for producing monochloropentanes were found to be a temperature above  $200^{\circ}$  in absence of light or catalysts. On the large scale, a stream of electrolytic chlorine is passed into a very rapid stream of the heated vapour of the pentanes, and the hydrogen chloride evolved is absorbed in water. The hydrolysis of the amyl chlorides is carried out by hot aqueous caustic soda, the resulting sodium chloride solution being again electrolysed. The chlorination of *n*-pentane yields about equal proportions of primary and secondary amyl chlorides (3-chloropentane predominating in the latter); *iso*-pentane gives 85 per cent. of primary *iso*-amyl chlorides and 15 per cent. of tertiary amyl chlorides.

(v.) Addition of halogen is not so widely practised technically as substitution, but an important example consists in the addition of chlorine to acetylene,<sup>51</sup> which is hardly safe on the large scale, except when aided by catalytic action. Whilst iron, aluminium, or sulphur chlorides are stated to be useful for this purpose, the most suitable compound is antimony pentachloride, which forms moderately stable addition compounds with both dichloroethylene  $\text{CHCl} : \text{CHCl}$  and tetrachlorethane  $\text{CHCl}_2 \cdot \text{CHCl}_2$ .

Tetrachlorethane has useful properties as a solvent, etc., but is surpassed by trichloroethylene,  $\text{CHCl} : \text{CCl}_2$  (Westrosol), in solvent power, stability and convenience of boiling-point. Fortunately the latter compound can be obtained in over 80 per cent. yield when tetrachlorethane (100 parts) is heated with slaked lime (60 parts) and water (50 parts), and it is manufactured by this means on an extensive scale. The tetrachlorethane is manufactured by passing acetylene and chlorine alternately into a solution of antimony pentachloride in the product itself. In the first phase, the tetrachlorethane is converted into dichlorethylene :—



whilst subsequently the latter compound is re-converted into tetrachlorethane :—



At suitable intervals the passage of gas is suspended whilst the tetrachlorethane produced is removed by fractional distillation. By this means acetylene and chlorine are never actually brought into contact in the free condition, and a somewhat dangerous process becomes quite safe.

### (c) Actions of Oxidation.

Four typical processes may be selected from a large number in order to illustrate the technical applications of catalytic action in the oxidation of organic derivatives in the liquid condition, as distinct from the gaseous oxidations dealt with in Section II., Chapters IX. and X. (pp. 242 and 263).

(i.) An important use of oxidising catalysts is the addition of lead, manganese or cobalt “driers” to linseed and other oils which are to form the basis of paints and varnishes, or of linoleum or other oxidised fatty-oil products. Modern driers consist of salts of one or more of these metals with linoleic acid (unsaturated fatty acid) or abietic acid (rosin acids), whilst formerly the practice was simply to add to the heated oil a mixture of the oxides, or frequently lead oxide alone. The amount of metallic oxide present is greater in the older process than in the modern method.

The highly unsaturated glycerides of linseed and similar oils absorb oxygen on simple exposure to air, but at first very slowly (*i.e.*, there is a marked “period of induction”); the initial oxygen addition-product, however, acts as an excellent catalyst for further addition of oxygen, which then proceeds more rapidly and steadily. The function of the metallic salt “driers” consists in eliminating the induction period and rendering possible a free absorption of oxygen from the commencement.

The structure of the oxidised glycerides, which are generically termed "linoxyn," is complex; a fuller description than space permits here, both of the abundant studies of the mechanism of oxidation of the drying oils and of their technical manipulation, may be found in the works to which reference is made in the bibliography to this chapter.<sup>52</sup>

(ii.) Toluene can be converted into benzaldehyde by oxidation with precipitated manganese dioxide in presence of moderately concentrated sulphuric acid. Appelbaum<sup>53</sup> finds that the oxidation is accelerated by the addition of a small proportion of ceric or ferric sulphate, and has patented an apparatus for the continuous production of benzaldehyde by this means, the benzaldehyde and toluene being removed by steam, and unchanged toluene fractionated and returned continuously to the charge in the reaction-vessel.

(iii.) Aniline Black, the important dyestuff produced by oxidation of aniline, is conveniently prepared by treating a solution of aniline hydrochloride in water, at ordinary temperatures with the theoretical amount of sodium chlorate, if small quantities of salts of certain metals are also present.<sup>54</sup> For this purpose vanadium or osmium compounds are the most active, whilst cerium salts or copper sulphate are also effective.

(iv.) Mercuric salts are frequently useful catalysts in oxidation processes, especially when the oxidation is effected by sulphuric acid (which is reduced to sulphur dioxide). The original commercial method of manufacture of phthalic anhydride from naphthalene, for example, consisted in heating the hydrocarbon with sulphuric acid at 250° or above in presence of about 1 per cent. of mercuric sulphate. The mercury salt increases the rate of oxidation very markedly, and, in consequence, minimises the production of sulphonated derivatives and other by-products. This example is well known as one of those instances in which the discovery of the catalytic method (in 1896)

was fortuitous, the acceleration having first been observed owing to the accidental breakage of a thermometer in a batch of naphthalene which was being oxidised by sulphuric acid alone.<sup>55</sup>

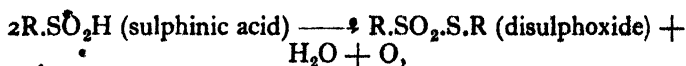
(d) **Catalysis in the Preparation of Organic Sulphur Compounds.**

(i.) *Sulphonations*.—Mercuric sulphate is also useful in directing the course of sulphonation of the more complex aromatic hydrocarbons and derivatives. Thus, in presence of about 0.5 per cent. of this salt, anthraquinone yields a mixture of 1:5- and 1:8-anthraquinone disulphonic acids ( $\alpha$ -substituted), whereas, in its absence, the products are the  $\beta$ -substituents, 2:6- and 2:7-anthraquinone disulphonic acids.<sup>56</sup> Mercuric sulphate also acts as a directive catalyst in the sulphonation of benzene derivatives.<sup>57</sup>

Again, in the  $\alpha$ -substituted sulphonic acids the sulphonic acid group can be replaced by hydrogen, in many cases, by boiling with dilute sulphuric acid, if mercuric sulphate is also present.<sup>58</sup>

(ii.) *Thio-compounds*.—Catalytic action is prominent in many of the reactions of organic compounds, containing bi- and quadri-valent sulphur, and although many of these are not much used at present in technology, it would appear that their importance may increase in the near future, especially in connection with problems associated with the vulcanisation of rubber.

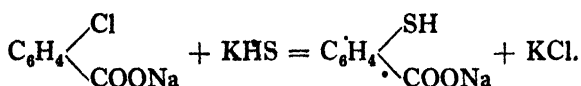
Thus iodine (or hydriodic acid) has an appreciable accelerating influence on the production of certain polythioderivatives,<sup>59</sup> e.g., in the action



and also in some cases of sulphonation<sup>60</sup> (e.g., benzenesulphonic acid).

Again, copper, or salts of copper, exert an effect<sup>61</sup> on the condensation of aromatic chloro-derivatives

with alkali sulphides or hydrosulphides of a similar nature to that mentioned above (p. 435) in the action of ammonia on chloro-derivatives; sodium *o*-chlorbenzoate, heated at 150°–250° with twice its weight of potassium hydrosulphide in presence of about 0.1 per cent. of precipitated copper, passes smoothly into sodium thiosalicylate :—



(iii.) *Accelerators in the Vulcanisation of Rubber.*

—The combination of sulphur with caoutchouc to form the resilient commercial product may be effected by mastication and heat-treatment with sulphur, or by alternate exposure of the rubber in solution to hydrogen sulphide and sulphur dioxide by the Peachey process. In either case the progress of the vulcanisation is aided to a marked extent if a fractional percentage amount of one or other of numerous compounds known as “rubber accelerators” is present. The theoretical significance of what takes place in the vulcanisation, and of the exact function of the accelerator, is not yet clear, and it is natural, therefore, that the quest for accelerating catalysts should still remain to a certain extent empirical. The literature of the subject is very large, and dozens of new accelerators are patented every year; reference should be made to the Reports of the Progress of Applied Chemistry issued annually by the Society of Chemical Industry, whilst the list of papers given at the end of this chapter<sup>63</sup> will afford some guidance to the main lines on which enquiry has been conducted in the past few years.

The utility of accelerators has been known since the earliest days of vulcanisation, when it was observed that mild alkalies, such as magnesia, lime or litharge, and also the proteins present in raw rubber, increased the speed of vulcanisation. The modern forms of

accelerators, however, date from about 1913, when Bayer and Co.<sup>62</sup> patented the use of organic bases with a dissociation constant greater than  $1 \times 10^{-8}$  (e.g., piperidine, benzylamine, *p*-phenylenediamine, etc.). These can be used at a concentration of 0.5 per cent. or less, whereas the amount of inorganic base employed was usually at least ten times this proportion.

As indicated, the investigations on organic rubber accelerators have been increasingly numerous since this date, and classes of compounds other than organic bases have been proved to be very serviceable. The chief general types of compound so far noted as efficient catalysts for this purpose include:—

- (a) Organic bases of the type of piperidine ;
- (b) Nitroso-compounds of the type of nitroso-dimethylaniline ;
- (c) Diphenylguanidine and other substituted guanidines ;
- (d) Thiourea and substituted thiocarbanilides ; arylthiazoles, especially in the form of mercapto-derivatives ;
- (e) Zinc or lead salts of dialkyldithiocarbamic acids, or of dithiobenzoic acid ;
- (f) Condensation-products formed between two of the classes: organic bases, nitroso-derivatives, thio-compounds.

Whether all these variants are necessary, or which, if any, is the most efficient, does not appear yet to be decided. The object in view is to secure maximum rapidity of vulcanisation with no accompanying undesired side-effects, and with the minimum addition of accelerating catalyst. The importance of this aspect of the rubber industry may be judged (bearing in mind that the average proportion of organic accelerator present does not reach 0.5 per cent.) by the fact that, in 1923, the annual world consumption of synthetic accelerators for rubber was estimated at over 2,000 tons.





## CHAPTER V

### CATALYTIC POLYMERISATION, OF ORGANIC COMPOUNDS

POLYMERISATION processes are becoming increasingly important in industrial organic chemistry, and in many cases the polymerisation is accelerated by means of catalysts. It has therefore seemed desirable to devote a separate chapter to an outline of the chief instances in which catalytic polymerisation is employed in technical practice. At the same time, it has not been felt necessary to give an exhaustive account of industrial processes involving polymerisation, not only from considerations of space, but also because in many cases catalysts are not indispensable and in many others they play a far less vital *rôle* than in those processes which have been described in the earlier chapters of this book. We shall restrict ourselves, therefore, to a brief description of four industrial applications of catalytic polymerisation, namely, the production of (i.) synthetic rubber, (ii.) resins from coumarone, indene and styrene, (iii.) lubricants, and (iv.) motor fuel. These four applications, broadly speaking, illustrate the main types of polymer that are obtainable according to the nature of the raw material and the degree of polymerisation.

Many unsaturated compounds exhibit to a greater or lesser extent the phenomenon of auto-condensation, or polymerisation. In some cases, such as in the polymerisation of formaldehyde to paraformaldehyde and the polyoxymethylenes, the action is reversible, *i.e.*, the polymer can be de-polymerised to yield the original substance. The polymerisation of unsaturated hydrocarbons (the object of most of the industrial processes) is, however, never truly reversible, and in many of these processes polymerisation is accompanied

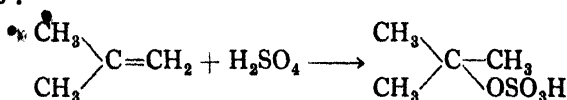
or followed by other reactions such as cracking, ring-closure, and condensation with other molecules present in the original material.

In many cases polymerisation proceeds slowly under ordinary conditions and can be accelerated by moderate increase in temperature, increased pressure, exposure to ultra-violet light or other radiation, or by the presence of catalysts.

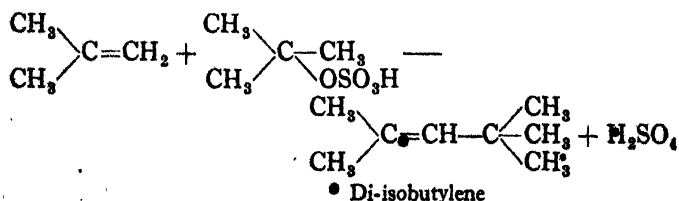
Among the materials frequently employed as catalysts are the mineral acids (notably sulphuric acid), the anhydrous chlorides of aluminium, zinc and iron, metallic sodium, oxygen and peroxides, and porous materials such as active carbon, silica gel and activated earths.

### The Theory of Polymerisation.

The nature of polymerisation, as also the function of catalysts in the process, is still only imperfectly understood. Polymerisation in the presence of sulphuric acid was considered by Kondakov<sup>1</sup> to proceed through the intermediate formation of the alkyl sulphonic acid, thus :—

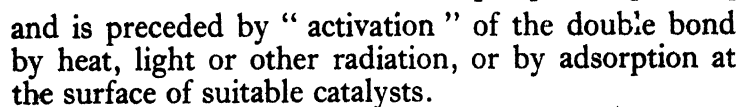


which then reacted with another molecule of olefine in the following manner :—



Polymerisation in the presence of anhydrous metallic salts, such as aluminium chloride, undoubtedly involves the formation of organo-metallic complexes which appear during the reaction as dark, pasty masses, insoluble in light netroleum. and which on treatment

The conclusions drawn from modern physico-chemical studies <sup>2</sup> and from the more purely chemical work of Staudinger and his co-workers <sup>3</sup> indicate that polymerisation is a "chain" reaction, proceeding by successive additions of monomer to the growing polymer. The process commences with the formation of the dimer, which does not as a rule itself polymerise, but reacts with another mole of monomer to form a trimer, and so on. Staudinger has shown that in the case of styrene, polymers containing as many as 5,000 styrene units may be built up in this way. The addition takes place through the double bond in the following manner :—



The tendency of olefines to polymerise increases with increasing molecular weight from ethylene upwards, but reaches a maximum with the hexenes and

heptenes. It is considerably increased by the proximity of other double bonds as in the case of conjugated di-olefines, and by that of negative groups such as phenyl (*e.g.*, styrene), halogens (vinyl halides) and acidic groups (vinyl esters).

#### (1.) Synthetic Rubber.

The story of the numerous attempts to synthesise rubber or suitable substitutes is a long and somewhat romantic one, and we can only refer briefly to it here.

Although Greville Williams<sup>5</sup> first showed that isoprene ( $\beta$ -methyl butadiene, obtained by the destructive distillation of natural rubber) could be polymerised to a spongy substance resembling rubber, the credit for the first synthesis is usually accorded to Tilden.<sup>6</sup> Tilden found that isoprene obtained by the destructive distillation of turpentine, when subjected to the action of light, hydrochloric acid or nitrosyl chloride, was polymerised to a material closely resembling rubber. The best results were obtained, however, by subjecting the oily product resulting from heat polymerisation of isoprene to the catalytic treatment. This observation was confirmed later by Ostromislensky and Koschelev,<sup>7</sup> who found that at 80°–90° isoprene polymerised to  $\beta$ -myrcene (the dimer) which yielded a satisfactory rubber-like product when treated at 60°–70° with sodium and barium peroxides.

Kondakov<sup>8</sup> reported the formation of a rubber-like product by the polymerisation of 2 : 3-dimethyl-1 : 3-butadiene in the presence of alcoholic potash, and many other workers (Wallach, Lebedev, Collie) obtained similar products by the polymerisation of other conjugated diolefines.

Research along these lines was considerably stimulated after 1905 by the rapid rise in the price of natural rubber, and one of the most important discoveries made was that of Mathews and Strange<sup>9</sup> concerning the catalytic action of metallic sodium. A similar discovery was made practically concurrently by

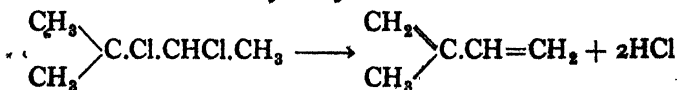
Harries.<sup>10</sup> The sodium remained for the most part unchanged at the conclusion of the reaction. Later, Harries<sup>11</sup> summarised the principal methods of polymerising the butadiene hydrocarbons to artificial rubbers as follows :—

(a) Heating alone or in acetic acid solution in a sealed tube at 60°–100°.

(b) Heating or allowing to stand in the presence of metallic sodium in an atmosphere of carbon dioxide.

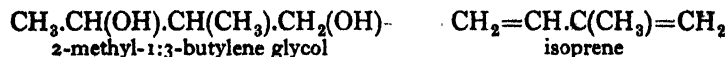
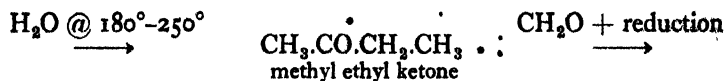
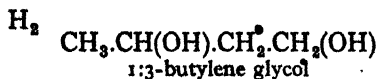
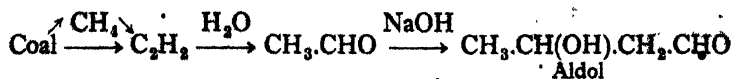
(c) Heating in the presence of peroxides, *e.g.*, benzoyl peroxide.

Although these synthetic products possess many of the attributes of natural rubber, and can in fact be vulcanised and processed in a similar manner, they are not, even in the case of the isoprene products, identical with the natural material. Furthermore, despite claims for the production of rubber substitutes from a wide variety of diolefines, the possibilities are in practice limited to butadiene and its simple homologues, isoprene, piperylene, and 2 : 3-dimethyl-1 : 3-butadiene. The success of a synthetic rubber process consequently depends to a large extent on the availability of these compounds, and many elaborate syntheses have been worked out for their preparation. Suitable aliphatic alcohols or chloro-compounds are frequently suggested as raw materials ; thus, a number of syntheses depend upon the removal of hydrogen chloride from trimethylethylene dichloride :—



The trimethylethylene can be prepared by the pyrolysis of monochloropentanes in the presence of barium chloride at 300°–450°,<sup>12</sup> or by the dehydration of amyl alcohols. During the war of 1914–1918 the Bayer Co. manufactured 150 tons a month of “methyl rubber” from 2 : 3-dimethyl butadiene synthesised from acetylene *via* acetone and pinacol. In the more modern synthetic rubber process of the I.G. combine, isoprene

is synthesised from acetylene (derived from coal) by the following steps <sup>13</sup> :—



Since the war there has been a considerable renewal of interest in synthetic rubber, particularly in Germany and the U.S.A. In the former country coal forms the basic raw material, and in the latter the gaseous by-products of the petroleum industry. Modern practice favours conducting the polymerisation in colloidal solution, with careful control of the acidity of the reacting mixture. Thus, in one example, isoprene is treated with a colloidal suspension or solution of egg albumen, sodium oleate or turkey-red oil in the presence of electrolytes, together with compounds, such as perborates, which readily yield oxygen. The product is rolled into sheets with sulphur, and vulcanised in the ordinary way; the resulting material is said to possess high strength and elasticity.<sup>14</sup> In another similar case isoprene is polymerised by heating with water or caustic alkalis at 100° in the presence of alkali metals, acids, oxidising and emulsifying agents, and with a buffer system of  $p_H$  4.5–5.0.<sup>15</sup>

It has been stated that the synthetic rubber process has been brought to such a high state of efficiency in Germany that the country could readily become independent of the imported natural article. It has also been reported that a synthetic rubber industry is being organised in Russia.

It is evident that the synthetic rubber processes are akin to the "petrol-from-coal" projects, in that they appeal primarily to the non-rubber growing countries, and whilst appearing uneconomic under normal peacetime trade conditions, assume considerable importance in time of war.

(ii.) Polymer Resins.

*Coumarone Resins.*—The resins known to industry as the coumarone resins are the product of the polymerisation of coumarone, indene, or their homologues, present in the "heavy benzol" or "solvent naphtha" fractions of high-temperature coal tar. They have received wide application, and are employed in such diverse products as chewing gum, printing ink, varnish, linoleum and waterproofing preparations. Although many catalysts have been suggested for the polymerising process, sulphuric acid is the only one which is used to any extent in industry. The action of sulphuric acid on these compounds was discovered by Kraemer and Spilker in 1890.<sup>16</sup>

The general type of process is as follows: coal-tar naphtha is fractionated and a fraction, b.p.  $160^{\circ}$ – $185^{\circ}$ , is separated, washed free from acids and bases, dried and polymerised with sulphuric acid under carefully controlled conditions of temperature and rate of heating. The resulting tar is settled and the clear resin solution separated, washed free from acid and dried. Oil is distilled off under reduced pressure, any naphthalene is removed by steam distillation, and the molten resin is poured into suitable moulds. The highest grade resins are produced at the lowest polymerising temperatures, and hence rapid cooling of the reaction vessel is essential. Numerous patents have appeared for methods to achieve these conditions. In a typical example for the continuous manufacture of coumarone resins, the naphtha and acid (3 per cent. of 95 per cent. sulphuric acid) are allowed to flow between rapidly revolving surfaces in the form of vanes moving between



fixed baffles, or of a conical rota moving in a fixed cone. With a clearance of  $1/10$ – $1/200$  in. between fixed and moving surfaces the reaction is complete in about 10 seconds.<sup>17</sup>

The colour of the resins varies from pale yellow to dark brown, the quality depending not only on the conditions of polymerisation but also on the proportions of coumarone, indene and other resinifiable constituents of the naphtha fraction used.

*Styrene Resins.*—The technical styrene polymers, produced by the action of heat, light or various catalysts, are transparent vitreous substances, insoluble in water, alcohol or petroleum fractions but soluble in aromatic hydrocarbons, esters and halides. They form valuable synthetic plastics which find application in the manufacture of cast, moulded and lathe-turned articles and coating materials. They have also been added, either before or after a preliminary hydrogenation treatment, to lubricating oils to improve the viscosity characteristics of the latter.

Styrene occurs to a small extent in the products of coal carbonisation, but has recently been made available in quantity (although it is still somewhat costly) by the pyrolysis of ethyl benzene<sup>18</sup> or of its chlorinated derivatives. Ethyl benzene can be readily prepared by the catalytic condensation of ethylene and benzene.

Polymerisation proceeds by exposure to heat or light, but is markedly accelerated by the presence of catalysts such as sulphuric acid<sup>19</sup>; a satisfactory, hard resin can be produced by the action of 85 per cent. acid at  $0^{\circ}$ .<sup>20</sup> Metallic sodium or potassium,<sup>21</sup> anhydrous metallic halides and aryl diazonium fluo-borates,<sup>22</sup> and a wide variety of other materials have been cited as catalysts for the technical polymerisation of styrene.

Numerous other unsaturated substances have been polymerised to yield technically useful resins. Among the most important of these are the vinyl esters, *i.e.*, the esters of the hypothetical vinyl alcohol,  $\text{CH}_2=\text{CH.OH}$ . Vinyl acetate, prepared by passing

acetylene into acetic acid containing mercuric sulphate (*cf.* p. 374), can be polymerised by the action of heat, light, traces of oxygen, or catalysts such as barium peroxide to give vitreous resins used in the manufacture of moulded articles, lacquers, safety glass, coating preparations, adhesives, etc. Further information concerning these and other polymer resins should be sought in the well-known monographs on the subject.<sup>23</sup>

(iii.) The Production of Lubricating Oils by Polymerisation.

The possibilities of using as lubricants the viscous oils formed when ethylene and higher olefines are polymerised by treatment with aluminium chloride or similar catalyst has attracted attention for similar reasons to those obtaining in the case of synthetic petrol and rubber. Good lubricants are essential for the modern internal combustion engine, and the search for synthetic methods of production has become intense during the last ten years or so. Suitable sources of olefines for the purpose are found in the gases resulting from the cracking of liquid and gaseous hydrocarbons, coal gas, and low-boiling unsaturated spirits from various sources, for example, that produced from water-gas by the Fischer process (*cf.* Section II., Chapter III., p. 119).

Ipatiev and Rutala<sup>24</sup> showed that hydrocarbons of very high molecular weight resulted when ethylene was treated with aluminium chloride at 0° under pressure. Other workers found that anhydrous ferric and zinc chlorides behaved in a similar manner but required the use of higher temperatures. The production of viscous oils suitable as lubricants by the aluminium chloride polymerisation of ethylene was described by Stanley, Nash and Bowen.<sup>25</sup> Dunstan, Hague and Wheeler<sup>26</sup> showed that by varying the temperature, pressure, catalyst, and time of contact, products ranging from higher (gaseous) olefines to lubricating oils could be obtained by polymerisation of ethylene. Otto<sup>27</sup>

has claimed that high-grade lubricating oils can be prepared by the polymerisation of ethylene at 100–200 atmospheres pressure at room temperatures in the presence of gaseous boron trifluoride.

The liquid olefines in cracked gasoline<sup>28</sup> and in light oils from coal<sup>29</sup> can be similarly converted into satisfactory lubricants by aluminium chloride treatment. A survey of such methods of production is given by Sullivan and co-authors,<sup>30</sup> who also describe a method of polymerising the olefines resulting from the cracking of paraffin wax: crude wax is cracked at 510°–540° and atmospheric pressure, and a distillate of end point 260° is separated from the products and polymerised by stirring with anhydrous aluminium chloride (50 g./gal.) for 18 hours at 99°. The stirring is then stopped, the tar settled and withdrawn, and the oil steamed until the desired viscosity is reached. In a typical trial, 10 per cent. of light distillate, 80 per cent. of lubricating oil and 10 per cent. of tar were obtained.

The addition of finely divided aluminium or zinc to the aluminium chloride is claimed by Imperial Chemical Industries Ltd.<sup>31</sup> to increase the yield of lubricating oil, and the same company advocates the treatment of olefines at 150° and 70 atmospheres pressure, in the presence of florida earth impregnated with finely divided nickel and aluminium chloride.<sup>32</sup>

The oils produced by these methods are said to be characterised by good viscosity curves, low pour-points, good colour and stability towards oxidation.

#### (iv.) The Production of Polymer Petrol.

One of the most recent applications of catalytic polymerisation to industry is the production of high-grade petrol from natural and refinery gases by the polymerisation of the olefines at low temperatures (200°–280°) and pressures (ca. 200 lb./sq. in.) in the presence of solid phosphoric acid catalysts.

The process has been developed mainly by Ipatiev, Egloff and the Universal Oil Products Company of America, where the process has been successfully tried out on a commercial scale. Some idea of the possibilities of the process will be gained from the statement (by Egloff) that in 1935 there was a potential supply of 9 billion gallons of polymer petrol from all refinery and natural gas. The modern internal combustion engine (particularly the aircraft engine) is tending to require fuel of increasingly high anti-knock properties and, since it is possible by the polymerisation process to produce petrols with an octane number of up to 100, it is probable that the process is destined to be of considerable importance.

Early experiments of Ipatiev<sup>33</sup> showed that ethylene, at 70 atmospheres pressure and at temperatures above 325°, readily yielded light oils consisting of higher olefines, paraffins and cycloparaffins. Dunstan, Hague and Wheeler<sup>26</sup> also found that, together with other products, low-boiling hydrocarbons of high anti-knock value could be obtained by catalytic polymerisation of ethylene.

The type of catalyst employed by Universal Oil Products consists of a calcined mixture of pyrophosphoric acid and a solid absorbent such as kieselguhr,<sup>34</sup> or is prepared by heating a mixture of phosphoric acid and kieselguhr to 180°–500° and then rehydrating by heating in steam at a high temperature.<sup>35</sup> The I.G. Company<sup>36</sup> have patented the use of liquid acids of phosphorus in the presence of heavy metals, acid esters of phosphoric acids, or solutions of an anhydride of an acid of phosphorus in a liquid acid of phosphorus.

In one of the recently erected U.O.P. plants,<sup>37</sup> cracked gas containing 25–30 per cent. of propylene and butylenes, under a pressure of 200 lb./sq. in., is passed at the rate of 125,000 cu. ft. per hour through a gas-fired preheater where the temperature is raised to 205°. The hot gas then passes through a series of

four towers, 3 ft. 6 in. in diameter and 25 ft. high, containing the solid phosphoric acid catalyst. The polymerisation is exothermic and a temperature rise of about  $55^{\circ}$  takes place. The reaction products pass through a condenser to a receiver where separation of liquid and residual gas takes place. A yield of 5 gallons of petrol (octane number 81) per 1,000 cu. ft. of intake gas is obtained. When approximately 20 gallons of polymer petrol have been produced per pound of catalyst, the catalyst in one tower is regenerated *in situ* by passing a calculated amount of air through it. The oxygen burns off the highly polymerised deposits and restores the catalyst to its original activity. The main use of the polymer petrol is in blending with low-grade spirits to increase their anti-knock properties.

It is possible to fractionate the cracking gases to obtain a fraction containing only butenes and butanes, and by selective polymerisation the iso-butene can be converted into di-isobutene which upon mild hydrogenation is converted into "iso-octane gasoline" with an octane number of 96-100. • •

The polymer petrol, although still highly unsaturated, contains paraffins and cycloparaffins in the lower fractions and aromatic hydrocarbons in the higher fractions. It is evident, therefore, that polymerisation is accompanied or followed by other reactions such as cracking and ring closure, and probably also condensation with non-olefinic constituents of the raw gas. •



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